THE CHEMISTRY of PAINTS and PAINT VEHICLES

Clare H. Hall

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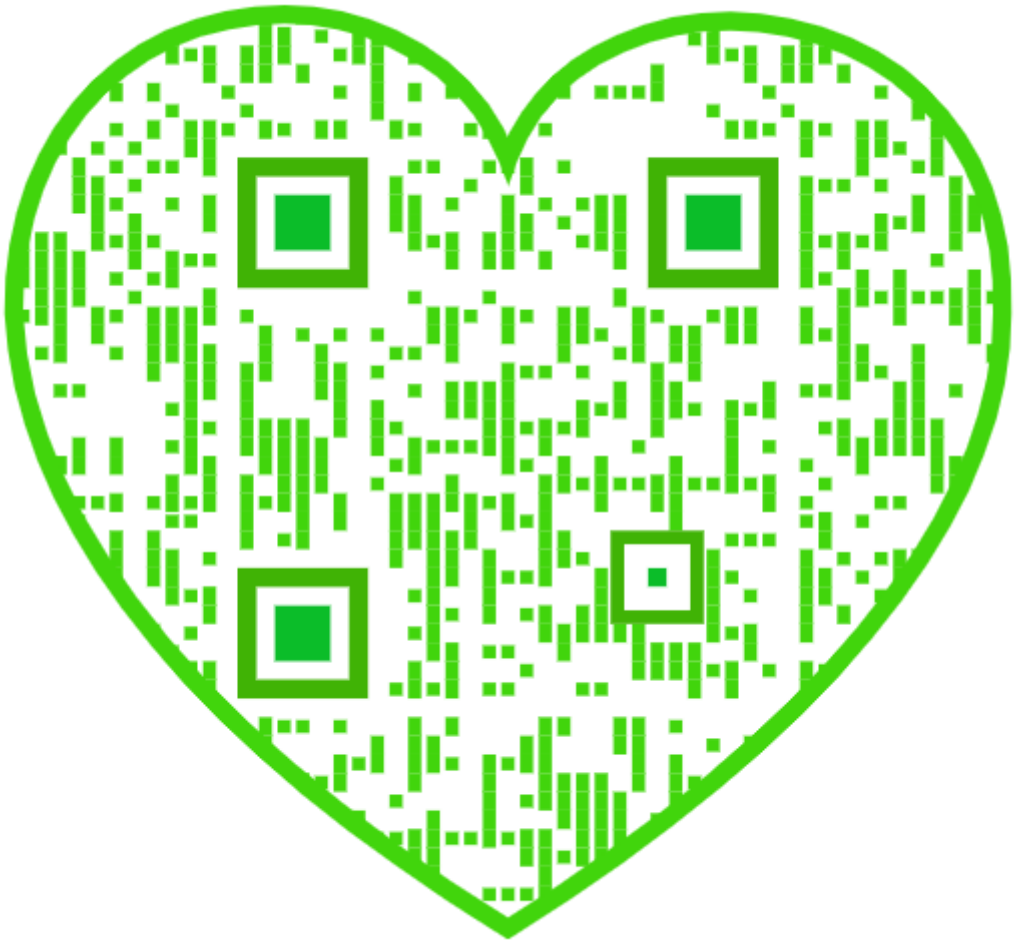
NEW YORK



THE CHEMISTRY OF PAINTS AND PAINT VEHICLES

BY

CLARE H. HALL, B.S.

Chemist for The Chas. Moser Co.

NEW YORK

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PREFACE

In writing this book the author has attempted to sift from the great mass of analytical chemistry those methods which apply particularly to the analysis of paints, at the same time calling attention to the most important physical characteristics of the raw materials. No chemist can be proficient in the analysis of paints without a thorough knowledge of all the materials with which he comes in contact, and although no attempt is here made to give anything more than the most general facts regarding them it is to be hoped that such will be sufficient to act as an incentive for each to personally investigate all pigments, etc., until thoroughly familiar with their every aspect.

The general scheme which the author has attempted to follow is to take up in Chapter I the elementary constituents of paints with the quantitative methods for their determination; in Chapter II the dry materials entering into the manufacture of paints with a short description of their physical properties and the separation of their elementary constituents by methods given in Chapter I; in Chapter III the analysis of samples consisting of a mixture of two or more of the raw materials described in Chapter II; in Chapter IV an interpretation of results previously obtained where it

is desired to duplicate the sample analyzed; and finally, in Chapter V, descriptions and methods for determining the purity of paint vehicles.

The close connection between the facts treated in the first three chapters has made it impossible to separate them by very definite lines of demarcation. This necessitates their overlapping, especially in the case of Chapters II and III.

This book being written from the standpoint of a chemist employed in the manufacture of paints and colors, Chapter IV has been included in an attempt to bridge the space between the laboratory and factory. It is here that so often the results of previous analysis are rendered worthless by being placed in the hands of one who does not understand their interpretation nor the composition of the raw materials which he is using. Over this work the chemist should have final supervision.

CHAPTER I

THE DETERMINATION OF THE ELEMENTARY CONSTITUENTS OF PAINTS

ALUMINIUM

A. I. **Determination as Oxide.** — If NH_4Cl is not already present, add it to the solution in moderate quantities, then NH_4OH in slight excess. Boil until no odor of ammonia is perceptible. Let settle, decant the supernatant liquid onto filter and repeat several times. Finally wash the precipitate on filter until free from chlorides; dry, ignite, and weigh as Al_2O_3.

A. II. **Separation of Aluminium from Iron.** — Precipitate with NH_4OH as in A. I. Wash, filter, dry, ignite, and weigh combined oxides. Now fuse with KOH in a silver crucible in order to dissolve the Al_2O_3. Digest fused mass in water and wash the residue of Fe_2O_3. Dissolve in HCl, and reprecipitate with NH_4OH, in order to free the iron from potassium salts, then dry, ignite, weigh, and get Al_2O_3 by difference.

BARIUM

B. I. **Determination as Sulphate.** — Heat the solution, which should not contain too much free acid,

then add excess of hot dilute H_2SO_4, and keep the mixture near the boiling point for some time. Decant supernatant liquid onto Gooch crucible, and boil the precipitate with water. Finally transfer and wash on Gooch crucible with hot water until filtrate shows no turbidity with $BaCl_2$. Dry, ignite, and weigh as $BaSO_4$.

Separation from Calcium. — See C. II.

CALCIUM

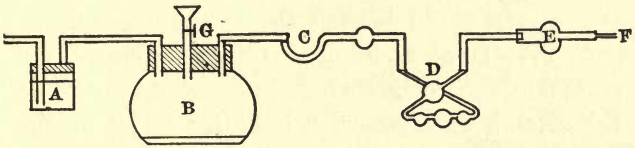
C. I. **Determination as Oxide.** — To the boiling solution made alkaline with NH_4OH, add an excess of boiling ammonium oxalate. Boil or keep near boiling-point for some time, then let settle, filter, and wash with boiling water until free from ammonium salts. Dry, transfer to platinum crucible, and ignite over blast lamp for fifteen minutes; weigh, and again ignite for five minutes. If there is any change in weight, ignite again to constant weight. Where the quantity of calcium is small one ignition will usually suffice. Weigh as CaO.

C. II. **Separation from Barium.** — Precipitate combined calcium and barium with ammonia and ammonium carbonate. Filter on a Gooch crucible, dry and ignite at a very gentle heat, adding a small amount of ammonium carbonate to convert any CaO to $CaCO_3$. Weigh the combined carbonates; dissolve in HCl, filter out asbestos, dilute highly, boil, and precipitate barium with a very dilute

solution of hot H_2SO_4. Decant on filter, wash with hot water and HCl to dissolve any traces of calcium sulphate that may have precipitated, and determine barium as in B. I. Calculate $BaSO_4$ to $BaCO_3$, and get $CaCO_3$ by difference.

CARBON

C. III. Determination of Carbon Dioxide.



APPARATUS. — A is a bottle containing potash which serves to prevent any CO_2 from the air entering the apparatus, and through it air is drawn into the flask B, in which the carbonates are decomposed. B contains a stoppered funnel tube G, and is connected with the calcium chloride tube C, which serves to prevent moisture from entering the potash bulbs D. E is another calcium chloride tube and is connected with the aspirator at F.

PROCESS. — Place weighed sample (5 gms.) in flask B. Now carefully weigh the potash bulbs (they should be stoppered with short pieces of glass rod), and then connect the apparatus as shown above. Add water to the flask B through G, and draw a current of air, about one bubble per second, through the apparatus. Next add acid slowly

through G, closing the cock after each addition, meanwhile heating the flask gently, and slowly increasing flow of air. When no more action is produced by the further addition of acid, remove all CO_2 from the apparatus by suction, then remove potash bulbs, restopper them with stoppers formerly used, and after thirty minutes weigh and get CO_2 by increase in weight.

CHROMIUM

C. IV. **Determination as Chromic Oxide.**— All chromate compounds must first be changed into the chromic state, which is indicated by an intense green color, without any red or yellow. If not already in this condition add a small amount of HCl and boil until the change is complete. Add NH_4OH in slight excess and boil until supernatant liquid is colorless; then wash precipitate ($Cr_2(OH)_6$) by decantation several times and transfer to filter, dry, ignite, and weigh as Cr_2O_3. If filtrate is yellow it indicates that the chromate has not been completely reduced.

Separation from Iron and Mn. — See I. II. and M. III.

C. V. **Chromates Soluble in Water.** — When a chromate compound soluble in water is digested with HCl the following reaction takes place: —

$$K_2Cr_2O_7 + 14HCl = 2KCl + Cr_2Cl_6 + 7H_2O + 6Cl.$$

If potassium iodide is present each atom of free Cl will replace an equivalent of I, and the liberated

iodine may be titrated with a standard solution of sodium thio-sulphate ($Na_2S_2O_3$). The application of these reactions to the determination of chromium is as follows: Place a weighed quantity of the chromate in a flask with water and an excess of potassium iodide. When dissolved add an excess of HCl, then cork the flask tightly and allow the mixture to digest at gentle heat for some time, cool, uncork, wash into a beaker and titrate with standard sodium thio-sulphate, using starch solution as an indicator.

The n/10 sodium thio-sulphate solution may be made as follows: Dissolve 24.822 gms. of c.p. transparent crystals in one liter of distilled water at 15.5° C. This is best checked by standardizing against n/10 $K_2Cr_2O_7$ made by dissolving 4.913 gms. c.p. $K_2Cr_2O_7$ in one liter of distilled water at 15.5° C.; 25 c.c. $K_2Cr_2O_7$ are treated as above with KI and HCl. The I liberated is titrated with the $Na_2S_2O_3$ solution, using starch solution as an indicator. When the $Na_2S_2O_3$ solution is added in sufficient quantities to take up all free iodine present the blue color caused by free iodine in the presence of starch will disappear. The green color due to chromic salts must not be confused with the blue. A very little practice will enable the operator to distinguish between them. The strength of the thio-sulphate solution may now be calculated, remembering that each atom of free Cl in above equation releases one atom of I. It will be found

more convenient to express results as 1 c.c. $Na_2S_2O_3$ = x gms. $K_2Cr_2O_7$ and 1 c.c. $Na_2S_2O_3$ = x gms. I.

The first equation is used to calculate the strength of all chromate solutions, while the second is used in calculating free iodine, as in the iodine absorption method.

As the $Na_2S_2O_3$ solution changes on standing it should be restandardized with n/10 $K_2Cr_2O_7$ at frequent intervals. The change will be greatly or wholly reduced by keeping in a dark place and protecting from the air by means of a layer of kerosene.

If insoluble chromates, such as $PbCrO_4$ are to be determined, this process must be slightly varied as boiling with HCl is necessary to effect complete decomposition. In such cases proceed as in the determination of MnO_2 by the Bunsen Method. (See M. IV.)

C. V. a. **Chromates Soluble in Water.** — Such as $Na_2Cr_2O_7$ and $K_2Cr_2O_7$ are readily analyzed by dissolving in water, adding a small amount of dilute HNO_3, and precipitating with lead nitrate or acetate. The $PbCrO_4$ thus formed is washed, filtered on a Gooch crucible, and dried at a low temperature to constant weight. From the weight of the $PbCrO_4$ present the per cent Cr_2O_3 or $Na_2Cr_2O_7$ may be readily calculated.

IRON

I. I. **Determination as Ferric Oxide.** —Oxidize any ferrous iron to ferric, precipitate with NH_4OH

in excess, boil, filter, wash, dry, ignite filter and precipitate separately, and weigh as Fe_2O_3.

I. II. **Separation from Chromium.** — Proceed as directed in I. I. Fuse the weighed oxides with two parts KNO_3 and four parts Na_2CO_3 in a platinum crucible. Treat the mass with boiling water in a beaker, adding a small quantity of alcohol and heat gently for several hours. Filter. The filtrate will contain all the chromate as alkali chromate, while the iron will remain as a residue on the filter. Wash the residue thoroughly, dissolve in HCl, reprecipitate with NH_4OH, filter, then dry, ignite, and weigh as Fe_2O_3.

Make the chromate solution acid with HCl, add more alcohol, boil to reduce chromic acids to chromic salts, and treat as in C. IV.

I. III. **Determination with Potassium Permanganate.** — The following method gives very rapid, accurate results but is used to advantage only when a number of iron determinations are to be made.

PERMANGANATE SOLUTION. — Weigh out 3.162 gms. c.p. $KMnO_4$ and dissolve in one liter distilled water at 15.5° C. Check the solution with n/10 oxalic acid solutions as follows: 25 c.c. n/10 oxalic acid are heated to 60° with H_2SO_4 present and the $KMnO_4$ solution added to faint permanent pink. From this the strength of the $KMnO_4$ solution is calculated and will generally be found the same as that calculated from the weight. The reaction that takes place is as follows: —

$$Mn_2O_7 + 5H_2C_2O_4 + 2H_2SO_4 = 10CO_2 + 2MnSO_4 + 7H_2O$$

Another method of standardizing the $KMnO_4$ solution is to titrate it against pure iron wire and thus find the equivalent of 1 c.c. in grams iron. To do this fit a rubber stopper with a bent delivery tube into a flask holding about 30 c.c. Clamp into a retort stand in an inclined position, having the tube so bent as to dip into a small beaker containing water. Fill the flask one third full with dilute H_2SO_4, add a little Na_2CO_3 and when the CO_2 gas evolved has driven out all the air, add 0.1 gm. pure iron wire to the contents of the flask and heat gently until dissolved. Then cool rapidly under a stream of water and add $KMnO_4$ solution to faint, permanent pink. Express results as 1 c.c. $KMnO_4$ = x gms. metallic iron.

To determine iron in any compound dissolve in HCl, reduce with metallic zinc in a flask or better by passing through a Johnes Reductor. Add H_2SO_4 and titrate with standard $KMnO_4$ solution as above.

It will be seen that this method also offers a very ready means for separating ferrous from ferric iron. After the total iron has been determined the ferrous iron is determined by dissolving without oxidation as with iron wire and determining the amount by titration with the $KMnO_4$ solution to faint, permanent pink. The difference between the amount of ferrous iron thus determined and the total

amount found will be the amount of ferric iron present.

Potassium permanganate solutions may be rendered stable by filtering through asbestos after preparation. Still more satisfactory results may be obtained by warming and allowing to stand two days before decanting and filtering. In case this is not done an unstable solution will result which must be restandardized whenever used if satisfactory results are to be obtained.

LEAD

L. I. **Determination as Sulphate.** — To the solution add H_2SO_4 in slight excess, and if HCl or HNO_3 is present evaporate to sulphuric acid fumes. Dilute highly with water and an equal volume of alcohol, filter on a Gooch crucible, wash with a hot mixture of equal parts water and alcohol, dry, ignite, and weigh as $PbSO_4$.

MAGNESIUM

M. I. **Determination as Magnesium Pyrophosphate.** — Make the solution alkaline with NH_4OH and if any precipitate forms add NH_4Cl until it is dissolved. Add sodium acid phosphate in excess, and stir the mixture, taking care not to touch the sides of the beaker with the stirring rod. Cover the beaker, and allow it to stand in a cool place for at least twelve hours, after which filter and rinse out the beaker with a portion of the filtrate. Now

wash precipitate with a mixture of three parts water, and one part ammonia water until the filtrate is free from sodium salts. Dry, and separate from the filter paper. Transfer the bulk of precipitate to a platinum crucible, burning the paper separately on platinum wire, and later adding the residue to the contents of the crucible. Put on the lid and expose for sometime to gentle heat, gradually increasing to intense redness. Cool, and weigh as $Mg_2P_2O_7$.

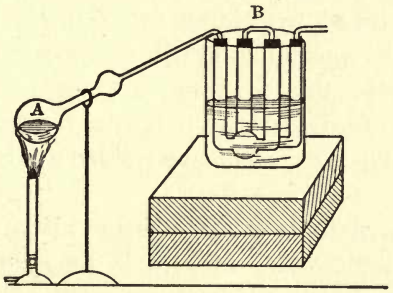
MANGANESE

M. II. **Determination as Mn_3O_4.** — Precipitate the solution, which should not be too concentrated, with NaOH or KOH. Boil, transfer precipitate to the filter and wash until free from alkali. Dry, separate from filter paper and burn paper separately as described above. Heat to constant weight and weigh as Mn_3O_4.

M. III. **Separation from Iron.** — Treat combined iron and manganese as in M. II., and weigh the combined oxides, then fuse with Na_2CO_3, dissolve the mass in HNO_3 and then boil, adding now and then $KClO_3$ crystals. The bioxide of manganese is formed and being insoluble in strong HNO_3 separates as a precipitate. When fumes cease with a slight explosion the manganese has been completely oxidized. Add a few more crystals of $KClO_3$, boil, filter on a Gooch crucible and wash with strong HNO_3. Transfer contents of crucible to a beaker and digest in HCl. Filter out the

asbestos, nearly neutralize with NH_4OH, then add some sodium acetate to precipitate any remaining traces of iron. Boil and filter. Heat the solution nearly to boiling and add an excess of microcosmic salt. Now make slightly alkaline with NH_4OH, boil, stirring until precipitate assumes the characteristic appearance of ammonium manganese phosphate. Treat the precipitate as in M. I., weighing as pyrophosphate ($Mn_2P_2O_7$). This method also can be applied to the separation of manganese from chromium and other metals of the third group.

M. IV. **Determination of Manganese Dioxide, Bunsen's Method.** — Place 0.4 gm. of the finely pul-



verized sample in the flask A, and pour over it concentrated HCl. At once connect A to B, in which is a solution of KI, the containing tubes being kept cool by filling the beaker about one half full of water. Now apply a burner to A and heat the solution until the sample is completely dissolved and all the evolved chlorine has been expelled and

driven into B. This requires but a few minutes. In order to prevent the iodine solution from being sucked back into the flask A, B is disconnected before the flame is removed from A. Titrate the free iodine in B with standard $Na_2S_2O_3$ as in C. V. From this calculate the amount of O released, and in turn the amount of MnO_2 present in sample. This method is also applicable to the determination of chromates insoluble in water, and to the determination of PbO_2 in red lead and orange mineral.

SILICON

S. I. **Silica and Silicates. Decomposition with Hydrofluoric Acid.** — The purity of silica may be readily tested by adding to the finely pulverized sample in a platinum crucible, concentrated hydrofluoric acid, then evaporating to dryness at gentle heat and finally igniting to intense red heat. When the sample is pure silica no residue will be left after ignition.

In the analysis of silicates the above process is varied somewhat. Proceed in the same manner, using, however, a platinum evaporating dish instead of a crucible, and before the HF has entirely evaporated, let cool, and add, very slowly, concentrated H_2SO_4 in sufficient quantities to convert all bases present into sulphates. Evaporate at a low temperature to sulphuric acid fumes. Let cool, and dilute with water. If the operation has been conducted properly there should be no residue

unless barytes is present, and in that case it will precipitate at once after diluting the concentrated H_2SO_4. If it is found present filter on a Gooch crucible, dry, ignite, and weigh as $BaSO_4$. The bases present will now be in solution as sulphates. Add NH_4Cl, then NH_4OH until alkaline, and treat any precipitate of aluminium as in A. I. If any iron is present (as in ochres) it may be separated from aluminium by A. II or I. III. To the filtrate add ammonium oxalate in excess, and if a precipitate forms, treat as in C. I. Test the filtrate for magnesium by M. I, and if found present determine accordingly. Finally obtain the quantity of SiO_2 present by difference after all other constituents including water have been determined. This method is applicable at all times to the analysis of silicates entering into the manufacture of paint, and offers a much better method for separation of silicates from barytes than does the method of fusing with Na_2CO_3.

S. I. a. **Decomposition with Sodium Carbonate in absence of Barytes.** — The following method is recommended for analysis of silicates where separation from barytes is not required since it gives SiO_2 direct, and not by difference.

Fuse a weighed quantity of the silicate with five or six times its weight of Na_2CO_3 in a platinum crucible over a blast lamp. When cool, dissolve the mass in an excess of HCl, evaporate nearly to dryness on a hot plate, then in drying-oven at 110° C.

for one hour. Add dilute HCl, warm, and decant the acid onto a filter. Again add acid and decant, and finally transfer the insoluble residue to the filter, and wash until free from alkali salts. Dry, ignite, and weigh as SiO_2. Examine the filtrate in the same manner as in S. I. for aluminium, iron, etc.

SULPHUR

S. II. **Sulphates. Determination as Barium Sulphate.** — Add to the boiling solution, which must not contain too much free acid (the presence of HNO_3 especially should be avoided), an excess of boiling barium chloride solution. Keep near boiling for some time, let settle, and decant the supernatant liquid onto a weighed Gooch crucible. Wash by decantation with boiling water, then transfer to the crucible, and wash until the last washings show no traces of chlorides with silver nitrate. Dry, ignite, and weigh as $BaSO_4$.

ZINC

Z. I. **Determination as Oxide.** — Heat the moderately dilute solution, which must contain no ammonium salts, nearly to boiling in a large beaker, and add Na_2CO_3 in excess. Boil, stirring occasionally, to avoid bumping. Allow the precipitate to settle, wash thoroughly by decantation onto a filter paper, repeat until the last washings are free from sodium salts. Dry and ignite the precipitate and filter paper together, and weigh as ZnO.

CHAPTER II

RAW MATERIALS, PROPERTIES, TESTS, AND METHODS OF ANALYSIS

The importance of the strength test in testing raw materials cannot be too strongly emphasized. All raw materials used should be analyzed, an OK sample kept, and the future shipments checked by the shade in oil, and by a strength test. This plan will be found much simpler and more satisfactory than an analysis, but it of course does not apply to whiting, barytes, and similar materials, which are used only as adulterants and have little body.

Strength Test. — Weigh out equal portions of the color to be tested, and the OK sample, and to each add equal portions of zinc oxide. Transfer each to a glass plate and rub with a spatula until well mixed. Now take a small portion, first of one then of the other, and rub on ground glass until there is no change in shade on further rubbing. (In the case of Prussian and Chinese blues, greens, and blacks, the mixture must be rubbed very hard for some time.) If the two shades are the same the sample is of proper strength.

Whites may be tested in a like manner by comparing the shade of the sample and the OK sample

in bleached oil, and by adding to equal portions of each equal portions of some color and treating as above. If the resulting tints are alike the sample is correct.

The relative value of a dry color may also be obtained by making a strength test between it and a sample of known purity, which has the same shade in oil and is made from the same materials. To do this weigh out equal portions of the known and unknown color (the amount will vary with the color and its purity; Chinese and Prussian blue and blacks about 0.2 gms., other colors much more, up to 1 gm., may be taken). Transfer each to a glass plate. Now weigh out two portions of 5 gms. each of zinc oxide, and add to the colors on the glass. Mix as described above and compare the shades on glass. If they are the same their value is the same, but if one is darker than the other add weighed quantities of the zinc oxide until the shades are the same after rubbing out thoroughly. The percentage difference in strength and value may now be determined. For instance: Color No. 1, to which 5 gms. of zinc oxide is added, gives the same shade as color No. 2 with 7 gms. of zinc oxide added. Then color No. 1 is only $\frac{5}{7}$ as strong as color No. 2, and has only $\frac{5}{7}$ of its value plus value of adulteration present.

BLUE PIGMENTS

Chinese Blue. — This pigment is made by precipitating a solution of yellow prussiate of potash

with copperas and then adding some oxidizing agent to convert the ferro-ferro-cyanide thus formed to the ferri-ferro-cyanide. It is a bulky pigment, very dark blue in shade with a decided bronze cast, but having a beautiful blue tint. The color is immediately destroyed by heat and fixed alkali, but is unaffected by acids. On the addition of alkali it breaks up into ferric hydrate and an alkali ferro-cyanide. On the addition of acid the color reappears.

Prussian Blue. — Prussian blue is very dark in color, with an intense blue shade in oil, and without the bronze cast of the Chinese blue. It is not as strong as the Chinese blue, and the tint is much inferior. It may be made from yellow prussiate of soda and in consequence costs less than Chinese blue.

These blues are very seldom adulterated dry, but when this is done, china clay, barytes, starch etc., are used. To test for starch, boil a sample with water, let settle, filter, and add a potassium iodide solution of iodine. The formation of a blue color is evidence of starch. For the determination of china clay and barytes, see Dry Colors, Chapter III.

It will always be found much more convenient to test blues by strength against pure samples of Prussian and Chinese blues than to attempt an analysis.

Ultramarine. — This pigment is a very permanent blue, much lighter in shade than either Prussian or Chinese blue, and of a much more brilliant

purple tint. It has about the same value as a tinting color, but cannot safely be used with lead compounds since it contains sulphur, and hence is likely to form the black lead sulphide. It is found in nature as the mineral *lapis lazuli*, but at the present time the artificial ultramarine made by heating together in a closed vessel aluminium silicate, sodium sulphate, soda, sulphur, and charcoal is used exclusively in paints. The resultant pigment contains SiO_2, Al_2O_3, Na_2O, SO_3, and S with traces of water, lime, iron, etc. The manner in which these materials are combined to produce the blue is not well understood.

The tone of the color varies from greenish to purplish, the analysis seeming to show that the percentage of silicon increases and the aluminium decreases from the green to the purple.

Ultramarine blue is not effected by heat or dilute alkali, but is at once destroyed by acid with the evolution of H_2S. This gives a ready method of distinguishing it from cyanogen blues. It usually contains about 42 per cent SiO_2 and 25 per cent Al_2O_3, though both these amounts increase and diminish through narrow limits in different shades. As one increases the other diminishes. Owing to its peculiar composition and to the fact that it contains soluble silicates the analysis of ultramarine blue becomes complicated.

METHOD OF ANALYSIS. — Weigh out 2 gms. sample, treat with dilute HCl, evaporate to dryness and heat

for one hour at a temperature between 110° and 120° C. Add a small amount of HCl and repeat. This renders all silicic acid formed insoluble. Treat with HCl, boil, decant on filter, and repeat. Wash residue free from acid, dry, ignite, and weigh as SiO_2. Examine for barytes, china clay, etc., by S. I. or S. I. a.

Make filtrate up to 500 c.c. Take 250 c.c., make alkaline with NH_4OH, boil, decant on filter, wash, dry, ignite, and weigh precipitate as Al_2O_3. Any calcium may be precipitated from filtrate with ammonium oxalate.

To the other portion of 250 c.c., after heating, add a boiling solution of $BaCl_2$ and determine sulphates in the usual manner. Calculate to SO_3.

To determine S, oxidize with fuming HNO_3, in a closed flask. Add some NaCl, evaporate to dryness, and heat at 110° to 120° for one hour. Treat with dilute HCl, re-evaporate and again treat with HCl, filter out SiO_2, and precipitate boiling with barium chloride solution as in the determination of sulphate. After subtracting sulphate existing as SO_3, calculate remainder to S.

Obtain Na_2O by difference after all other materials have been determined, or to the filtrate from the aluminia add an excess of H_2SO_4, concentrate, and evaporate to dryness in a platinum dish by carefully igniting at a low temperature just sufficient to drive off the ammonium salts and excess of H_2SO_4. Weigh the sodium as Na_2SO_4.

BLACK PIGMENTS

Ivory and Bone Black. — These pigments are combinations of carbon, hydrocarbons, water, and mineral matter; their value as pigments depends upon their blackness and strength. The presence of oily matter is detrimental, as it retards drying when mixed with oil. Test for this by dissolving out with ether. To make an ANALYSIS of these pigments, weigh out 1 gm. sample (in absence of carbonate) in a porcelain crucible, then place lid on so that there remains a very small opening, and ignite at low heat until no more vapor is driven off. Cool, weigh, and express difference as water and hydrocarbons. Again ignite, very strongly this time with the lid removed, until all the carbon is driven off. This further loss is expressed as carbon and the residue as ash.

These blacks are rightly used in carriage painting, or where an intense black is desired, and never for tinting purposes, owing to their weak tinting power.

Carbon Black, or Gas Black. — This pigment is not so black as the best grade of ivory and bone blacks, but as black as some of the cheaper grades. It is very bulky, 1½ lbs. requiring about 1 gallon of oil to grind to a paste. It is a combination of carbon and hydrocarbons, and, like ivory and bone blacks, should be as free from oily matter as possible since any large amount of this present not only impairs the drying property to a very great extent, but might make the pigment dangerous to store, owing to the possibility of spontaneous combustion.

Carbon black has a very strong tinting power, but gives a dirty brown tint when compared to lamp black, and on this account is little used for this purpose. It finds its chief use in the manufacture of black paints, where so intense a black as that given by bone and ivory blacks is not required. It may be assayed in the same manner as bone black, and should leave no ash.

Lamp Black. — This pigment has a dark gray shade in oil, and finds its chief use in tinting. With white lead and zinc, good grades of lamp black give a very clear bluish tone, and this should always be taken into consideration in comparing samples. Its shade in oil matters little, as, where a black for painting is desired, carbon or bone black may be used. In strength it is inferior to carbon black, but its superior tint more than makes up for this deficiency. It should always be used where clear tints are desired.

Like the other blacks it should be quite free from oily matter and should always be tested for this impurity. All other things being equal, the lamp black containing the least amount of oily material is to be preferred. Its absence, however, is not so important a matter in the case of lamp blacks as in the other blacks, since this pigment is generally used only for tinting purposes, and any oil in the small quantity of black used as a tinter will have little effect on the drying of the paint.

It may be assayed in the same manner as carbon black, and like the latter should yield no ash.

BROWN PIGMENTS

Umbers. — "Raw" umber is a natural earthy material, the shade of which varies greatly, owing to the wide variation in the proportions of MnO_2 and Fe_2O_3 which are contained in it. After calcining it assumes a darker, "warmer" color, and is known as **burnt umber.** Its value depends upon its shade, strength, and fineness.

METHOD OF ANALYSIS. — To determine the percentage of manganese follow M. II., using for a complete analysis 1 gm. of the substance. In the case of burnt umber long continued boiling with HCl will be necessary to effect solution, owing to the fact that oxides of iron and manganese are rendered difficultly soluble by calcining. After digesting in the acid, filter, then dry, ignite, and weigh the insoluble residue, and finally separate it by S. I. or S. I. a. (In the analysis of all earthy pigments where prolonged digestion is necessary to effect solution, it is best to evaporate to dryness, heat for one hour at 110° C., and again dissolve in HCl in order to render insoluble any silicic acid that may be formed by the decomposition of the silicates present.) Make the filtrate alkaline with NaOH then boil, wash thoroughly, filter, dry, ignite precipitate and paper separately, and weigh the combined oxides of iron and manganese, and finally separate by

M. III., or by other suitable methods. Precipitate the filtrate with ammonium oxalate, filter, and treat the precipitate of calcium oxalate by C. I.

Manganese present as MnO_2 may be determined by M. IV.

Determine CO_2 by C. III., using a separate sample of 5 gms.

Dissolve in HCl and determine SO_3 by S. II.

Usually all that is necessary to know about an umber is the percentage of constituents not MnO_2 and Fe_2O_3, so as to be able to make allowance for them when matching a sample of umber, or an umber tinted color. In the analysis, therefore, the oxides of iron and manganese may be discarded (or weighed together without separating) and only the other constituents determined.

Vandyke Brown. — This substance is largely organic and is found in nature. It also is manufactured by calcining organic matter of plant origin in a closed vessel and by mixing black pigments with red oxides and ochres. It resembles the blacks somewhat in composition, but contains a smaller percentage of carbon and a larger percentage of hydrocarbons, and these constituents, together with the earthy materials present, give it the color. Its ANALYSIS is rather complicated, but fair results may be obtained by a combination of methods applied to carbon black and umber. The CO_2 present must be obtained by C. III. on a separate sample. If not present the hydrocarbons are

obtained in the same manner as in blacks. To determine carbon in the presence of carbonates, the sample is dissolved in HCl, the insoluble carbon filtered on a Gooch crucible, dried, weighed, ignited until all carbon is consumed, again weighed, and carbon obtained by difference. The metals in solution in HCl should be determined as in the analysis of umber. Alkali carbonates will be found in some samples.

Graphite. — This material is found in nature and is an allotropic form of carbon. It is of a brownish gray color, very greasy to the touch, and the finer grades are used in lead pencils and lubricants. The grade used in paints contains a considerable percentage of silica, with small amounts of other materials. This substance is unaffected by all ordinary acids and alkalies, and by the weather. On this account it is largely used for coating structural iron work and ship bottoms, and for these and similar purposes it has proved to be superior to any other material.

METHOD OF ANALYSIS. — To get the percentage of graphite, boil with diluted HCl, filter on a platinum Gooch, dry in an oven to constant weight, ignite over blast until the graphite is driven off, and get graphite by loss. In the absence of carbonates the graphite may be estimated in the same manner as carbon in blacks. A platinum instead of a porcelain crucible should be used, however, and it will be found necessary to ignite the sample much longer and at a higher

temperature than in the case of blacks. A sample of from .25 to .5 gms. will be found more easily manipulated than 1 gm., owing to the less combustible nature of graphite. The non-combustible residue may be analyzed by S. I. or S. I. a.

GREEN PIGMENTS

Chrome Green. — This pigment is a mixture of chrome yellow and Chinese blue, and taking all properties into consideration it is the most satisfactory green made. The shade varies with the proportions of blue and yellow and with the method of making. Thus, a green made by precipitating a yellow made from acetate of lead on the blue has a yellowish shade and bluish tint, but if nitrate of lead and white lead are substituted for the acetate a bluish green with a yellowish tint is obtained. The finest greens are obtained by combining these two methods and by properly manipulating the materials used. The mere grinding together of blue and yellow will not produce shades which at all compare in brightness with those obtained by precipitating the colors together.

METHOD OF ANALYSIS. — The color of chrome green is, like that of Chinese and Prussian blue, immediately destroyed by fixed alkalies and heat. The usual adulterants are barytes, china clay, and very rarely whiting and gypsum. To estimate them, proceed as in Dry Colors. In case the percentages of yellow and blue are desired, determine the percent-

age of adulterants as in Dry Colors, and the percentage of yellow as in Chrome Yellow, and obtain the percentage of blue by difference.

RED PIGMENTS

Iron Oxide. — This material exists in nature as hematite and limionite and is the chief ore of iron. Many of the oxides on the market are obtained from the natural source and hence are found to vary widely in composition, some containing as little as 10 per cent ferric oxide, whereas others are practically pure. The shade will vary from a dull reddish brown (due to presence of MnO_2) to a bright reddish color. Very bright oxides are produced artificially by calcining copperas and may be procured pure.

The value of this pigment depends upon its shade in oil, percentage of oxide of iron, and its freedom from grit. ANALYZE as in *umber*, substituting NH_4OH in place of NaOH. The presence of any dye may be determined by adding alcohol to a small sample and observing whether or not any color is dissolved. If so the amount may be calculated by difference after all other constituents have been determined, or in the absence of combined water and carbonates by direct ignition. Alizarine is almost exclusively used for the production of Tuscan and Indian Reds. Zinc oxide may sometimes be found in both of these products.

Natural oxides are likely to contain traces of

phosphates, sulphides, etc., and to get an absolutely correct analysis should be treated as in the analysis of iron ores for smelting purposes. This involves much work, however, and the results are of no value to the paint maker.

VERMILION PIGMENTS

English Vermilion (HgS). — This pigment occurs in nature as the mineral cinnabar, but rarely of sufficient brightness to permit of its being used as a vermilion. The manufactured article is a very bright vermilion, but owing to its cost has been almost entirely displaced by the vermilion made from orange mineral. In permanency it is declared by some to be the best of the vermilions, but this is open to dispute. It is insoluble in all ordinary acids and alkali, and on burning leaves no ash, depositing metallic mercury near the top of the crucible, if not too hot. This gives a ready method of testing its purity, as any material added as an adulterant will be left behind in the crucible.

Red Lead and Orange Mineral Vermilion. — This vermilion, which has practically displaced mercury vermilion, is made by precipitating an eosine or scarlet dye (sometimes permanent red) on red lead or orange mineral. In the case of eosine it is precipitated with some lead salt, usually lead nitrate. The shade thus produced is superior in brilliancy to English vermilion, but is not at all permanent to light. Scarlet is precipitated with

barium chloride, and while this does not give so bright a vermilion as eosine it nevertheless gives a more permanent color, and is sometimes used for dark shades. Sulphate of barium must always be precipitated with the scarlet, otherwise an inferior shade is produced. Adulteration of these vermilions is usually made with barytes, but where a vermilion for dipping purpose is desired, china clay and whiting are used. For ANALYSIS see Dry Colors, Chapter III.

Permanent Red, Para Red. — This vermilion, which has recently been greatly in demand, is produced by diazotizing para nitranaline and combining with beta naphthol, usually on a barytes, whiting, or china clay base. Sometimes red lead, orange mineral, or zinc are used, but not as a usual thing. In the case of the pure color on barytes this pigment is superior to all other vermilions in permanency, but when mixed with orange mineral or zinc it loses some of this property. It is unaffected by dilute alkali and by dilute HCl and H_2SO_4, but is dissolved by acetic acid. Concentrated HCl dissolves it in small quantities, while with concentrated H_2SO_4 it dissolves to a deep purple, the color returning on diluting. If a small quantity of dry alkali is placed in a test tube with it, and some alcohol poured in, the same reaction takes place. For quantitative ANALYSIS see Dry Colors, Chapter III.

In addition to para nitranaline other diazotizable bases are treated and combined with beta naphthol

in a like manner. Of these, the ones generally used are; alpha naphtylamine, which produces a maroon; and ortho anisidine, which produces a light vermilion shade of red.

When it is desired to know what dye is present in a vermilion or red lake, it may be determined by the following tests: —

REAGENT	SOURCE OF COLOR				
	ALIZARINE	EOSINE	PARA NITRANALINE	ORTHO-ANISIDINE	SCARLET (2 R)
H_2SO_4 Conc.	Dark brown with reddish undertone becoming light yellow on diluting.	Changes to yellow. Fluorescent solution with excess of NaOH.	Purple. Color returning on diluting.	Purple. Red on diluting.	Darkened. Lighter on diluting.
HCl Conc.	Color becomes "Muddy."	Changes to yellow. Reddish fluorescent solution with excess of NaOH.	Color slightly darkened. Lighter on diluting.	Dark purplish red. Lighter on diluting.	Darkened. Lighter on diluting.
NaOH. Conc. sol.	Dark reddish brown. Little change on diluting.	Little change Fluorescent solution on diluting.	Color changed to brownish red Light red on diluting.	Little change.	Reddish solution on diluting.
Alcohol.	Insoluble.	Reddish fluorescent solution.	Slight yellowish, orange solution.	.....	Slight reddish solution.
NaOH Conc. and Alcohol.	Purplish, dark brown on diluting.	.....	Purple. Color returning on diluting.	Little change.	Color darker. Reddish solution on diluting.

American Vermilion, Basic Lead Chromate.— This vermilion is manufactured by heating together in water, white lead, sodium, or potassium bichromate and soda ash, until the color no longer change on further heating, and finally adding a small amount of sulphuric acid to brighten the shade. It has but little body or brightness, and owing to its peculiar crystalline nature has a tendency to settle rapidly in oil. It is very permanent, however, and on this account has been in considerable demand. Until recently it has often been used in conjunction with eosine vermilions, and when so used the resultant vermilion becomes very difficult to analyze, owing to the varying composition of both materials. For approximate analysis and separation of such a material see Analysis of Dry Colors. Since the introduction of Para reds, American vermilion has fallen into disuse.

WHITE PIGMENTS AND ADULTERANTS

Barytes ($BaSO_4$). — This material, which is the most widely used of any adulterant, is found in nature in large quantities as natural sulphate of barium. It is very heavy and on this account is much used for adulterating white lead. It does not grind well with oil, however, being " short," probably owing to its crystalline nature, and it has a tendency to settle into a very hard mass. On this account it is not advisable to use it in mixed paints.

Barytes has very little opacity, having no effect on the shade in oil of a strong color even when added in large quantities. It should be very white and without grit. It is insoluble in all ordinary acids and alkalies and in all concentrated acids except hot H_2SO_4, in which it dissolves again separating on diluting. For ANALYSIS boil one gram (1 gm.) in dilute HCl, filter, wash thoroughly, dry, ignite in porcelain crucible, and weigh the insoluble material, which will be $BaSO_4$, and any silica or silicates which may be present. The latter will rarely or never be present, but the insoluble residue may be tested by S. I. If any silica or silicates are present, even in small quantities, an effervescence will be noticed on the addition of HF and the bottom of the platinum crucible will become warm.

The filtrate may be tested by making alkaline with ammonia and boiling. A precipitate will be hydrates of iron and aluminium. Filter, dry, ignite, and weigh as Fe_2O_3 and Al_2O_3. It will not be necessary to separate or to make certain whether both are present. Test filtrate for calcium by precipitating hot with ammonium oxalate. Determine soluble sulphate by dissolving 1 gm. in HCl, filtering, and precipitating with $BaCl_2$, calculating the $BaSO_4$ thus produced to $CaSO_4$ by the proper factor. Any calcium not satisfied by the sulphate is, in the presence of carbonates, calculated to whiting ($CaCO_3$), or if no carbonates are present, to lime (CaO). Water and moisture are

determined by heating the original sample if carbonates are not present.

China Clay ($2SiO_2Al_2O_3+2H_2O$). — This is a light, bulky clay with but little opacity, being essentially a hydrated silicate of aluminium. It may be ANALYZED by S. I. or S. I. a, the percentage of free H_2O obtained by drying the sample at 100° and that combined by ignition of 1 gm. in a porcelain crucible, subtracting the amount found free.

When china clay is encountered in an analysis of a paint or dry color, this combined water must be taken into consideration and calculated from the per cent Al_2O_3 present, with which it seems to vary in a fairly constant ratio of about 1:3. Take a paste, for instance, in which 75 per cent of insoluble material has been found. After separating by S. I., 50 per cent $BaSO_4$ is found and 10 per cent Al_2O_3. This by difference gives us 15 per cent SiO_2. But in the added China clay there was an amount of water averaging $\frac{1}{3}$ of the Al_2O_3 present, which was lost on igniting the insoluble residue. So $\frac{1}{3}$ of 10 $=3\frac{1}{3}$, and our result of analysis of the insoluble material becomes

	50% Barytes
	$28\frac{1}{3}$% China clay
Total	$78\frac{1}{3}$%

China Clay is insoluble in ordinary alkalies and acids, but gradually decomposes into aluminium

sulphate and silicic acid with hot concentrated H_2SO_4.

Gypsum, Natural Sulphate of Calcium ($CaSO_4 + 2H_2O$). — A white mineral with trifling opacity, formerly used widely as an adulterant but at the present time very seldom encountered. Its ANALYSIS consists in determining the materials insoluble in acid, Fe_2O_3, Al_2O_3, CaO, SO_3, CO_2, and H_2O. When dehydrated it is widely used under the name of Plaster of Paris.

Carbonate of Magnesium ($MgCO_3$). — This is the lightest, most bulky white used. It is never encountered in mixed paints or pastes, and its use in all paint products is limited, but it is sometimes used in wood filters. Its ANALYSIS would consist in determining the CO_2 present by C. III., dissolving 1 gm. in HCl, and determining the insoluble material, Fe_2O_3, Al_2O_3, and calcium in the solution, and after these materials are precipitated treating the filtrate as in M. I. for magnesium.

Silicate of Magnesium. — A light, bulky silicate of no opacity, but used to a considerable extent to adulterate mixed paints. It is a chemical combination of MgO and SiO_2, usually in the proportion of 35 per cent MgO and 60 per cent SiO_2, with small quantities of Al_2O_3, Fe_2O_3, MgO, CaO, H_2O, etc. It does not grind readily with oil, unless a large proportion of the latter is present, and hence resembles barytes in this respect. It is insoluble in

ordinary dilute acids and alkalies. For ANALYSIS proceed as in S. I.

Silica (SiO_2). — A pigment without opacity, not much used in pastes or mixed paints, but forming a main constituent of iron and wood filters. Its value depends upon its whiteness and fineness. Silica containing much grit has a very bad effect upon the mills. Its purity may be readily obtained by S. I.

SUBLIMED LEADS AND ZINC

Sublimed Lead. — This material, which is found on the market as a substitute for white lead, is different from that material in a great many of its properties. It is less poisonous and less susceptible to the action of gases and impure atmosphere. The commercial article is made by volatilizing galena (PbS) and converting it by oxidation into $PbSO_4$. As it is nearly impossible to obtain galena free from sphalerite (ZnS), zinc oxide will always be found admixed with it. Oxides of lead also occur in this pigment in some peculiar form of PbO.

A sample analyzed by the author was shown to have the following composition:

$PbSO_4$ =	78.60%
PbO =	13.80%
ZnO =	5.50%
$ZnSO_4$ =	1.63%
H_2O =	.13%
Total	99.66%

The above analysis was made several years ago and the pigment as now produced shows zinc sulphate only in traces. The pigment necessarily varies somewhat from time to time in percentage of constituents. The manufacturers give the following as an approximate analysis:

$PbSO_4 = 75\%$ } Lead oxy-sulphate, or
$PbO = 20\%$ } Basic lead sulphate
$ZnO = 5\%$

It will be noted that the manufacturers claim that the lead oxide present is chemically combined with the lead sulphate in the form of basic lead sulphate. While there is some basis for such a claim the evidence is not at all conclusive.

Many obstacles have been encountered by the manufacturers in making this product satisfactory. They claim to have overcome them and the more extensive use of this pigment would seem to confirm their assertions.

Zinc Lead. — This is made from a combination of zinc and lead ores. Samples analyzed by the author had the following composition:

$PbSO_4$	54.48%	— 51.52%
ZnO	41.44%	— 47.12%
$ZnSO_4$	2.16%	— 0.85%
H_2O	.52%	— .18%
Total	98.60%	— 99.67%

The second analysis is the more recent. The present standard requires zinc sulphate to be present in quantities less than 1%.

This pigment falls about midway between sublimed lead and American zinc in its chemical composition, excepting that it is free from lead oxide. Although its use by many manufacturers is general, it probably finds its widest use in the manufacture of paste primers.

American Zinc. — This is made by roasting sphalerite (ZnS) and converting it into ZnO. It always contains small quantities of lead which occur with it in the ore. The following is the composition of two different grades as determined by the author, No. I. being the better and No. II. the inferior grade.

I.		II.	
Insol. matter	= 0.50%	Insol. matter	= 0.10%
$PbSO_4$	= 4.96%	$PbSO_4$	= 13.16%
ZnO	= 91.53%	ZnO	= 82.00%
PbO	= 1.67%	PbO	= 1.06%
$ZnSO_4$	= 1.42%	$ZnSO_4$	= 3.73%
Total	100.08%	Total	100.05%

The best grades of sublimed zincs are practically free from oxides of lead and are widely used for mixed paints. Pound for pound they have better body than white lead, but bulk for bulk their body is inferior. They are, on the whole, quite satisfactory pigments to use.

It is quite certain that the composition of all these sublimed products is more complex than is ex-

pressed by these analyses, traces of sulphides, sulphites etc., being present. Arsenic will generally be found, especially in zinc, but in too small quantities to admit of determination. The following method will fulfil all demands for their analysis:—

METHOD OF ANALYSIS. — Dissolve 1 gm. in boiling dilute HCl (see analysis of paste and tinted paints, Chapter III, for the proper mode of solution), filter, washing with boiling water until all lead chloride on filter is dissolved. There should be little or no insoluble material, but in case there is, dry, ignite, and weigh. If a globule of lead is found in the crucible, this shows that the sample has not been properly treated, and another sample must be taken. Heat filtrate until all the lead chloride is dissolved, make alkaline with ammonia, saturate with H_2S, and filter. The filtrate may be discarded, as calcium will never be found in these materials when dry. Dissolve the well washed precipitate of PbS and ZnS with concentrated HNO_3, using as little as possible, then wash thoroughly with hot water, let cool, add carefully 5 c.c. concentrated H_2SO_4, treat as in L. I. After filtering out $PbSO_4$, determine zinc in the filtrate by Z. I. Determine sulphates on a separate sample by S. II., deduct amount due to zinc sulphate present, calculate the remainder to sulphate of lead by proper factor, and calculate remaining lead sulphate to PbO by proper factor. Express zinc found as

ZnO after deducting zinc sulphate found by dissolving separate sample in a mixture of water and alcohol, filtering, and precipitating with $BaCl_2$. It is also well to test the merits of different grades of sublimed products by their action with gloss oil.

Rapid Method for Analysis of Sublimed Products. — Determine H_2O on a separate sample of 1 gm.

Boil 1 gm. with water to which a small amount of alcohol has been added. Determine sulphate in solution and calculate as $ZnSO_4$.

Determine total sulphate on a separate sample, obtaining insoluble impurities at the same time. Deduct amount sulphate previously found as $ZnSO_4$ and calculate remainder as $PbSO_4$.

Treat a separate sample of 1 gm. with a mixture of water, alcohol, acetic and sulphuric acid until all zinc is dissolved. Filter on Gooch crucible, dry, ignite, and weigh. Deduct amount of insoluble impurities previously obtained, the remainder being $PbSO_4$. Deduct $PbSO_4$ found as calculated from sulphate present, and calculate remainder to PbO. Obtain ZnO by difference, or precipitate with Na_2CO_3. Wash free from sodium salts, filter, dry, ignite, and weigh as ZnO.

All of the above determinations being made on separate samples, they can be carried on at the same time and results obtained quickly.

Whiting. — This material, which is the natural carbonate of calcium ($CaCO_3$), contains small

amounts of CaO, Fe_2O_3, Al_2O_3, $CaSO_4$, etc., and is as widely used as an adulterant as barytes, but as a usual thing only in paste and mixed paints, and very seldom in dry colors, excepting permanent reds. With pure linseed oil it is widely used in the manufacture of putty.

Whiting should always be carefully examined for lime. This, if present in any appreciable quantities, will be detrimental. To test for this, boil a sample with water, and add phenol phthalein indicator. If a red color is produced, the presence of lime is shown. This will often be found to be the cause of a light green or blue tint losing its shade in the can. The shade will generally regain its original color on drying after being painted out.

An ANALYSIS of whiting should be made in the same manner as gypsum.

White Lead. — This pigment is the most important and widely used white pigment with which the chemist and paint maker comes in contact. It is properly made by the old Dutch process of corroding the metallic lead with weak acetic acid and tannin bark, or some similar substance. It is used as the basis of all high-grade prepared paints, frequently in conjunction with zinc oxide.

It never will be found adulterated in the dry state. Its purity, however, may be tested by adding dilute acetic acid which should dissolve it and leave no residue. This acid also will dissolve any whiting or zinc present, and these constituents may be

tested for in the filtrate by first precipitating the lead with H_2S in dilute acid solution, then testing the filtrate after making alkaline with NH_4OH, for zinc with yellow ammonia sulphide in excess. If found, filter and test for calcium in filtrate with ammonia oxalate. Barytes and sulphate of lead are the materials chiefly used to adulterate white lead in paste form and may be readily determined. Pure white lead has the following composition:—

$$2PbCO_3, Pb(OH)_2.$$

It is a basic carbonate of lead, and not lead carbonate as it is usually called.

METHOD OF ANALYSIS. — To analyze a sample of pure white lead for its constituent parts, dissolve in acetic acid, precipitate with H_2SO_4, dilute highly, add an equal volume of alcohol, filter on a Gooch crucible, dry, ignite, and weigh as $PbSO_4$. Now determine CO_2 on separate sample of 5 gms., calculate from this the percentage of $PbCO_3$ present, and calculate remaining lead to $Pb(OH)_2$.

Analyze the adulterated samples of white lead as in tinted pastes and paints, Chapter III.

French Zinc, Pure ZnO. — This material is made from metallic zinc by heating in retorts until the zinc is volatilized, then bringing the fumes in contact with air and collecting the oxide of zinc thus formed in bags or chambers.

The material thus produced is put upon the market in two grades, green and red seal. The green

seal is the finer quality, being the whitest of pigments, and is much used in white enamels and interior finishes.

French zinc should contain no lead or other impurities except in traces, thus being as nearly pure as it is possible to obtain a commercial article. It should dissolve completely in dilute acetic acid, and yield no precipitate on the addition of sulphuric acid and alcohol. When the solution is made alkaline with ammonia and yellow ammonia sulphide added, the resultant precipitate should be pure white. The percentage ZnO may be determined by Z. I.

YELLOW AND ORANGE PIGMENTS

Chrome Yellow ($PbCrO_4$). — This pigment, which is made by precipitating a solution of some lead salt (usually lead nitrate, acetate or basic acetate) with sodium bichromate, is the most important yellow pigment in use. It adapts itself to a wide variation in shade, from the light lemon-yellow made by precipitating $PbSO_4$ in conjunction with the $PbCrO_4$ to the very deep orange produced by heat and the addition of alkali, which forms more or less basic chromate of lead. The tone also is widely varied in all the shades, the addition of nitric acid giving the yellow a much brighter cast, and when added in considerable quantities producing a very greenish tint in the light shades.

Pure chrome yellow should contain no foreign material excepting $PbSO_4$, which, however, cannot be considered an impurity, owing to the fact that it is a necessary adjunct in producing the light shades. It is soluble in HCl and HNO_3, producing an intensely green solution caused by the chromic salts, and this may, in the analysis of paints and dry colors, always be taken as indicative of the presence of chromate of lead, its presence in the case of vermilions being due to the presence of American vermilion.

METHOD OF ANALYSIS. — If a sample is adulterated the percentage of adulteration may be determined as in dry colors. For analysis of a pure sample boil with dilute HNO_3 and alcohol until the lead chromate is dissolved. Let cool, add 5 c.c. H_2SO_4, and evaporate to sulphuric acid fumes, then dilute with water and determine the lead by L. I. Determine the chromium in the filtrate by precipitating with ammonia and treating as in C. IV. Dissolve in HCl and determine SO_3 by S. II.

Red Lead and Orange Mineral (Pb_3O_4). — These materials are made by submitting lead or lead compounds to the action of heat and air; the former by oxidation of metallic lead, the latter by oxidation of white lead.

They will be found to vary in shade from the dull brownish yellow red lead of domestic manufacture to the bright bluish orange of the imported material. Their value depends upon their color and body and

they should always be tested for these properties. The body varies greatly and on this account the mere determination of the amount of Pb_3O_4 in a sample of vermilion made from them is not sufficient to properly match it. A special article on the matching of vermilions containing orange mineral will be found in Chapter IV.

The exact composition of red lead is a matter of much dispute. As a matter of fact the composition varies considerably, but it seems probable that Pb_3O_4 expresses the correct composition and that the variation observed is due to uncombined oxides of lead existing as an unavoidable impurity in the material.

The peculiar action of these compounds with rosin varnish and the prevention of it has troubled the paint and varnish trade for many years. The author obtained some results which may be found of interest from the paint standpoint, and the reader is referred to his article in the issue of The Paint, Oil and Drug Reporter, for Sept. 29, 1902.

Yellow Ochre. — Yellow ochre is an earthy pigment of very dull shade in comparison to chrome yellow. It is composed of a hydrated silicate of aluminium colored with iron, probably in the form of hydrated ferric silicate. Its value depends upon its strength and shade. It has fair body, and is much prized for primers, owing to its tendency to penetrate the wood, filling the pores. Its composition makes it permanent to all conditions of

the weather, and on the whole it is a very satisfactory pigment.

Dilute HNO_3 and HCl have little effect upon yellow ochres, except to dissolve very small amounts of iron. Concentrated HCl dissolves all iron completely on long digestion, leaving the white clay behind insoluble. Some aluminium may also be dissolved, and some silicic acid formed. It usually will be found to contain about 10 per cent combined water. Standard French washed ochre is generally considered as containing 20 per cent iron oxide calculated as Fe_2O_3. Its ANALYSIS may be made by S. I. or S. I. a., separating iron and aluminium by an appropriate method.

Raw Sienna. — Raw sienna, like ochre, is an earthy pigment, being much deeper in color and varying considerably from the latter in composition. Like ochre, it owes its color to hydrated ferric oxide (with small amounts of manganese), but this is present in much larger quantities than in ochre. The American siennas usually contain dehydrated ferric oxide in combination with the hydrated oxide, and this gives them a much redder tone than the Italian siennas and at the same time increases their opacity.

Burnt Sienna. — This is prepared by calcining the raw sienna at moderate heat until it has acquired the desired shade. The sienna then assumes a reddish yellow shade which is very transparent. The change in shade caused by calcining all earthy

materials is due to the driving off of the combined water, thereby changing the hydrated ferric oxide to ferric oxide.

Siennas are ANALYZED in the same manner as umbers and oxides, or may be treated by S. I. or S. I. a.

CHAPTER III

THE ANALYSIS OF DRY COLORS, PASTES, AND LIQUID PAINTS

Treatment of Sample. — In case of pastes and liquid paints take enough of the sample to permit of all necessary future tests and for analysis, put it in a suitable glass and add benzine. In the case of colors in japan and varnish, first wash thoroughly with turpentine before adding benzine, as the latter is liable to precipitate any gums present on the pigment, in which case they will not redissolve. (The turpentine should be added slowly with constant stirring.) Set the sample aside and let settle until the benzine is clear, then decant, adding fresh benzine and repeating until the color is free from oil. The color should be allowed to settle completely before the benzine is decanted, otherwise some of the lighter materials which do not settle readily may be lost, and thus the sample finally obtained will not represent the true proportions of constituents.

Dry the sample in an air oven, grind with a spatula on a rough filter paper until it is thoroughly homogenous and pulverized. If it is properly washed and not dried too long it readily forms a

fine powder. If any particles of dried oil or skin are observed, pass the sample through an 80-mesh sieve. This, however, should be avoided as much as possible by taking the sample of paste from below the surface, if the surface is at all dried.

Some chemists make a practice of using a centrifugal machine in separating the color from the naphtha, but this will not be found so convenient as the above method. Where great haste is desired this plan has its advantages, but the author finds that by using a vessel for washing of sufficient size, only two washings are necessary to free the pigment from oil, and ordinarily this may be accomplished in the course of an hour. With very light pigments, however, which stubbornly stay in suspension, the centrifugal machine is necessary to make haste.

Qualitative Tests. — Test for barium and calcium by means of the flame test. To do so, clean a platinum wire thoroughly by repeatedly heating and moistening with HCl, then moisten with HCl, touching it to the sample so as to collect a small amount on the wire, and place in the flame. A yellowish red flame, which quickly disappears, shows calcium. If barytes is present a greenish flame will appear. Again moisten with HCl, burn, and the flames will appear again, the green of the barytes showing much clearer this time. If this is repeated several times the calcium flame will be found to disappear entirely, but the wire must be moistened and burned

several times before the barytes flame finally fails to appear. With this test barytes can be detected in very small quantities. In the case of calcium, however, especially if very little is present (under 5 per cent), its presence might occasionally be overlooked and hence is best checked by the usual qualitative method.

The presence of gypsum which, however, is at present very seldom encountered in samples, complicates the analysis somewhat, and where it is suspected (only where sulphates are encountered in considerable quantities) it should be tested for by Thompson's method as follows: Treat about 1 gm. of the sample with 20 c.c. of a mixture of 1 part HNO_3 (sp. gr. 1.2) and 9 parts alcohol, and let stand for twenty minutes. Decant, and repeat washings three or four times with the same mixture. Any calcium carbonate together with white lead and zinc will be dissolved, while the gypsum will remain behind with the insoluble material which may be examined for calcium. In the absence of $CaSO_4$ all calcium may be considered present as $CaCO_3$.

Sulphates are tested for qualitatively by dissolving in HCl, filtering and testing the filtrate with $BaCl_2$ as in the determination of sulphuric acid. (See S. II.) As sulphates will almost always be found in paste and liquid paints in varying quantities, it will generally be found more convenient to make this test a quantitative one, and thus two

samples of the insoluble residue will be obtained, one of which can be tested for the presence of silicates by adding HF to it in a platinum dish, evaporating and noting whether there has been a loss in weight. If not, the insoluble material is pure barytes; if there has been a loss it will indicate silica or silicates (generally the latter) and the insoluble residue from the other weighing may be treated by S. I.

Carbonates will be shown by effervescence on the addition of acid. Lead and zinc need not be tested for qualitatively as their presence will be determined during the quantitative analysis. When H_2S is added to the alkaline solution the presence of lead will be indicated by the black precipitate (also caused by iron whose presence will be known by a reddish precipitate of hydrate when the solution is made alkaline). If zinc also is present the precipitate will be grayish and the zinc sulphide will have a tendency to remain in suspension. If it is absent the black precipitate settles very quickly, leaving a clear solution. The author only makes it a practice to make the flame test for barytes and calcium, the carbonate test (may be observed on adding acid to weighed sample for quantitative analysis) the test for gypsum when calcium is present and sulphates are found in any quantities, and tests to determine the character of the color when it may be due to different materials as in blue tints and vermilions. For qualitative tests for

these materials see Ultramarine and Permanent Vermilion, Chapter II.

Quantitative Analysis. — In taking a sample for analysis it is best to weigh out exactly one or two gms., avoiding fractional weights. With a little practice this becomes easy and it facilitates the work later on, since it does away with the necessity of keeping a record of the weight taken and of many subsequent calculations.

As a solvent dilute HCl, or in the absence of lead sulphate, dilute HNO_3 with a small amount of alcohol added, may be used. (The mixing of alcohol with HNO_3 should be accompanied with great caution.) In case dilute HCl is used care must be taken not to mistake the lead chloride which is likely to form in the bottom of the beaker when the solution is not dilute enough or becomes cold with any insoluble material present. It should always be made a point to burn the filter paper with the insoluble residue, and in case any lead has been left undissolved it will appear as a metallic globule in the bottom of the crucible surrounded by yellow oxide. The author uses HCl almost entirely in dissolving paints and dry colors, and has always found it very satisfactory when properly manipulated.

1. *Analysis of Dry and Untinted Paste Colors including chrome yellow, chrome green, cyanogen blue, and vermilions. Other colors should be treated according to methods given in Chapter II.*

Greens and cyanogen blues must be weighed

in a porcelain crucible and ignited gently to break up the insoluble blue (ignition must be at a low temperature, otherwise it will be found almost impossible to dissolve the Fe_2O_3 thus formed). For permanent reds, see 1. a. All that is required here is to obtain the percentage of adulteration, the color being calculated by difference.

METHOD.—To 1 gm. of the sample add concentrated HCl, then about five times as much H_2O. Boil until the color is dissolved and all the lead converted into lead chloride, which can easily be distinguished from any insoluble barytes, china clay, or silicate of magnesium by its crystalline character. If enough water is present it will all dissolve on boiling. Filter, and wash with boiling water until certain that all chloride of lead is washed out. The residue may be barytes, china clay, or silicate of magnesium. Test and separate by S. I. or S. I. a. (See also Qualitative Tests.) Heat the filtrate until any lead chloride which may have separated on cooling has dissolved, then add NH_4OH until alkaline, and saturate with H_2S. Heat on a hot plate, let settle, filter, wash thoroughly, and determine any calcium in the filtrate by C. I. This is rarely found in the above dry colors unless present as an impurity in the other adulterating materials, but is generally found in impure pastes. If carbonates are not present calculate any calcium to $CaSO_4 + 2H_2O$. If carbonates are present determine and calculate to whiting, then any remaining

calcium to gypsum. If the absence of gypsum is shown by the qualitative tests, the determination of CO_2 is unnecessary and the CaO present can be calculated to $CaCO_3$ by the factor 1.784. Subtract total adulteration found from 100.00 to determine the percentage color present.

Note. Mixtures of oxides, ochres, umbers, and siennas are (in the absence of zinc and lead) analyzed in the same manner as in *umber*, Chapter II, determining silica and silicates, Fe_2O_3, MnO_2, H_2O, $CaCO_3$, etc. Any gas or lamp black is determined by an appropriate method and expressed as C. When chrome yellow or chrome green is present the above method may be followed. If a separation of the color is desired, the precipitate of sulphides is dissolved in HNO_3, and lead separated and determined in the usual manner. Mn, Fe, and Cr are determined in the filtrate, and Cr separated and calculated to $PbCrO_4$. Any remaining lead is (in the absence of white lead) calculated to $PbSO_4$, and any remaining sulphate to $CaSO_4$ if calcium is present. If no calcium is present all sulphate is calculated to $PbSO_4$, the remaining lead to $PbCrO_4$, and from this the Cr_2O_3 calculated and subtracted from the total oxides of Mn, Fe, and Cr, in which case the separation of chromium is unnecessary.

1. a. With permanent red the process is a trifle different. In the absence of china clay and red lead dissolve in very dilute HCl. The barytes and

red will remain undissolved. Filter on a Gooch crucible. Dry in air oven to constant weight, then weigh, ignite, and weigh barytes, getting dye by difference. This gives very good results when the acid used is properly diluted and the digesting not continued for too long a time. When china clay is present (very rarely the case) the results cannot be depended upon, as there is a loss due to the water it contains. The Al_2O_3 must be obtained as in S.I. and china clay, the per cent water estimated, subtracted from the total loss on ignition, and the remainder expressed as the amount of dye present. This, however, will give only approximate results in many cases. If Pb_3O_4 is present it will generate Cl by acting on the HCl, and this will have a tendency to destroy the dye and lower the result. In such cases the dye must be obtained by difference after the other constituents have been determined (or in the absence of carbonates and combined moisture by direct ignition). This also will generally lead to an error by giving too high results, but by taking an average of the amount determined, and that calculated by difference, a result will generally be obtained by which the sample can be matched correctly. A special discussion on this point will be found in the matching of vermilions. (See page 69.)

When red lead is present without any white lead, sublimed lead, or zinc, determine as $PbSO_4$ by dissolving the precipitate of PbS in HNO_3 and treating

as in L. I. If white lead and lead sulphate are present but no calcium, determine CO_2 and SO_3 present, then convert to white lead and sulphate of lead, calculating any remaining lead as red lead. In case whiting also is present first satisfy it with CO_2, calculate the remaining CO_2 to white lead, any SO_3 present (in absence of gypsum) to $PbSO_4$, and the remaining lead to Pb_3O_4. If zinc is present it is obtained by treating the filtrate from the $PbSO_4$ in the same manner as described under the analysis of sublimed lead, Chapter II.

Such complications as the above will rarely or never occur, although permanent red pastes very often prove to be the most complex mixtures with which the paint chemist comes in contact, and often to determine the manner in which the materials present are combined is a very difficult matter.

In scarlet and eosine vermilions, if a complete analysis is desired, determine what dye is present by the table given under Permanent Reds, Chapter II. (See page 29.) Treat 1 gm. as in dry colors, first getting the adulteration as there described, but vary the process by dissolving the precipitate of PbS in concentrated HNO_3 as in permanent reds, and determine the lead present as $PbSO_4$ by L. I., calculating it to Pb_3O_4. The dye may then be obtained by difference, which yields results close enough for purposes of matching. White lead, sublimed lead, or zinc occasionally may be found in

eosine and scarlet vermilions. In this case treat as above in Permanent Reds. In case of a mixture of Pb_3O_4 and American vermilion determine total lead as $PbSO_4$ and total chromium as Cr_2O_3. Multiply Cr_2O_3 by 8.02 and express result as American vermilion. Divide this result by .883 and subtract from total $PbSO_4$ found, calculating remainder to Pb_3O_4.

2. *White and Tinted Paints containing no Calcium.* — Dissolve 1 gm. in dilute HCl as in 1. Filter, wash, dry, ignite, and weigh the insoluble residue. The residue may be barytes, china clay, or silicate of magnesium. (Any lead sulphate which has not been completely dissolved will be shown here as a metallic globule in the bottom of the crucible.) Separate the residue by S. I. or S. I. a. If china clay is found its combined water must be calculated and added to it as explained under China Clay, Chapter II. Add 5 c.c. concentrated H_2SO_4 to the filtrate, evaporate to concentrated sulphuric acid fumes and determine lead as in L. I., then make alkaline with ammonia and boil. The precipitate may be hydroxides of Fe, Cr, and Al, all coming from the tinters of the paint (or Al_2O_3 from the adulterating materials). This precipitate is usually discarded, as the tinters are customarily calculated by difference, but any chromium present may be determined at this point by separating as in I. II., calculating to $PbCrO_4$, this being calculated to $PbSO_4$ and this subtracted from the total lead determined as $PbSO_4$.

The filtrate now contains any zinc that may be present. Saturate with H_2S, boil, let settle, filter. If but a small amount is present and absolute results are not required, dry, burn, let cool, add a few drops of concentrated HNO_3, dry, and ignite for the second time at high heat, and weigh as ZnO. This will give results a trifle high, owing to the fact that all sulphur cannot be removed by burning. The error is not large, however, pure ZnO showing 101% zinc oxide by this method where 99.8% is shown when precipitated as carbonate. If the amount present is large and very accurate results are desired, wash precipitated ZnS free from ammonium salts, dissolve in HCl and determine zinc by Z. I.

In white paints the filtrate from the lead determination should be precipitated directly with Na_2CO_3, as the absence of Cr and Fe is assured.

Determine SO_3 on separate sample and calculate to $PbSO_4$.

Determine CO_2 on a separate sample and calculate to white lead. Any lead not satisfied (after calculating any Cr_2O_3 formed to $PbCrO_4$) is calculated as PbO.

3. *White and Tinted Paints containing Whiting without Gypsum.* — Dissolve in dilute HCl and proceed as in method 1, excepting that the precipitate of sulphides must be dissolved in concentrated HNO_3, washed thoroughly until the filter is free from acid, then 5 c.c. concentrated H_2SO_4 added

and the analysis continued as in method 2. Determine the calcium in the filtrate from the precipitate of sulphides, and calculate the resultant CaO to $CaCO_3$ by the factor 1.784. Determine SO_3 on a separate sample and calculate to $PbSO_4$. Calculate any lead not thus satisfied (in case of chrome yellow tints first determine $PbCrO_4$ and deduct from remaining lead) to white lead. This will give a result on white lead that is a trifle high, owing to the presence of oxides of lead in the sublime products present, but the error will be no greater than is made by determining the CO_2, calculating to whiting and calculating the remainder to white lead, since whiting is very liable to contain lime, thus causing the calculated white lead to be low. There is as much possibility of error in one method as in the other (not large enough to be of importance in either), and the former is to be preferred owing to the fact that one less determination is necessary. On the whole the determination of CO_2 may be dispensed with in nearly all analyses of paint samples without causing much error. Absolute results are very seldom required and are very seldom of importance, since in making up a sample to match the analysis an approximation only is attempted. A very close result should always be obtained on the percentage adulteration, but an error of one or two per cent on any white lead, zinc, or sulphate of lead matters but little, owing to the fact that they do not differ materially in cost.

4. *When Whiting, Sulphate of Lead, White Lead, and Gypsum are present* (a very unusual combination).—Determine whiting on a separate sample by Thompson's method. Determine SO_3 on separate sample. Proceed with the analysis as in method 3. Calculate the remaining calcium, not carbonate, as $CaSO_4+2H_2O$, then the remaining SO_3 to $PbSO_4$, and the remaining lead to white lead if $PbCrO_4$ is not present. In case chromium is present it may be determined as Cr_2O_3, then calculated first to $PbCrO_4$, this calculated to white lead and subtracted from the weight of white lead previously obtained. Or the CO_2 may be determined and whatever is left after satisfying the $CaCO_3$ may be calculated to white lead, any Cr_2O_3 present calculated to $PbCrO_4$, and any lead remaining besides the $PbSO_4$ previously calculated, expressed as PbO. This last result will be accurate only when the whiting present contains no CaO.

Note. Where great haste is necessary in making an analysis, variations of the foregoing methods may be used. Lead may be precipitated alone with H_2S in slightly acid (HCl) solution, redissolved in HNO_3 and determined in the usual manner. Or, where only present in small amounts and no great accuracy is required, the precipitate may be burned separate from filter paper, a small amount of HNO_3 added, evaporated to dryness, the residue ignited strongly and weighed as PbO.

This leaves all the third and fourth group metals

present in solution (with small amounts of lead, if the precipitation with H_2S has not been carefully performed). Third-group metals are separated by precipitation with ammonia and H_2S, leaving calcium present in solution. The precipitate is dissolved in HNO_3 or HCl, and iron, chromium, and aluminium precipitated with NH_4OH, leaving zinc in solution. This is precipitated and determined by an appropriate method.

Another method is to precipitate lead and all third-group metals with NH_4OH and H_2S, redissolve in HNO_3 determining lead as usual and obtaining calcium in filtrate. Zinc is obtained by dissolving the original sample in a mixture of alcohol and sulphuric acid. This will leave all lead behind as $PbSO_4$ as well as the greater amount of any calcium present. Iron and aluminium are precipitated with NH_4OH, and finally zinc by the addition of H_2S, or yellow ammonium sulphide.

Both these methods involve as much or more work than former methods given, but the necessity of waiting until lead is determined before determining third-group metals is avoided and considerable time saved.

Special

5. *Ochre Tints.* — Where ochre is used for tints it will remain behind with the insoluble impurities on treating with acid. The fact that ochre has no

standard of purity and is very much the same in composition as china clay makes a separation impractical. The author has found that the most convenient method is to digest the sample in dilute HCl and treat the filtrate by any appropriate method previously given. Excepting for a small quantity of Fe_2O_3 dissolved, the ochre will remain behind intact. Any barytes present is determined, subtracted from the total insoluble residue and the remainder expressed as ochreous material. To this must be added 10 per cent of its weight for combined water. The sample is then matched from the analysis by method 5, Chapter IV.

6. *Ultramarine Tints.* — As ultramarine contains in itself several materials used as adulterants, as well as soluble silicates, a paint in which it is used as a tinter must be analyzed by a special method. Dissolve 1 gm. in HCl, evaporate on a hot plate until nearly dry, then heat in an air oven at 120° C. (not above) for one hour after it has become dry. Boil with dilute HCl, decant on filter, repeat, and finally wash the insoluble material until free from acid. This residue will contain all the SiO_2 in the ultramarine as well as any insoluble adulterants. Separate by S. I. Determine the materials in the filtrate by an appropriate method. (Ultramarine tints will almost invariably be found free from lead, excepting what exists as an impurity in the zinc oxide used.) The percentage of ultramarine may be approximately determined by the percentage

of Al_2O_3 in the filtrate, but the author usually disregards it and matches sample by method 6, Chapter IV.

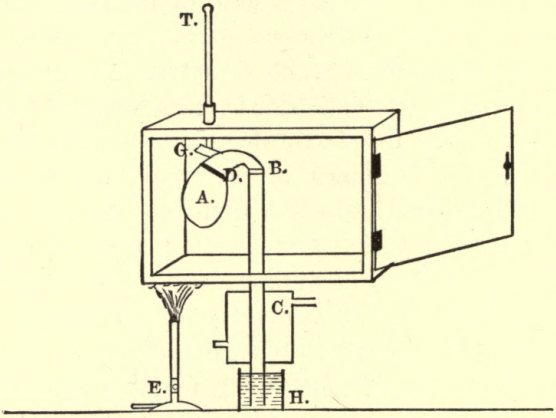
Mixed Paints

Determination of Pigment. — Many different methods are in vogue to accomplish this, mostly involving the use of an extraction apparatus. The following simple method is used by the author and gives very fair results: —

Measure off 25 c.c. of the thoroughly stirred paint in a pipette and transfer to a weighed 6-oz. beaker. Wash the pipette thoroughly with benzine, allowing the washings to run into the beaker. Fill with benzine and stir with a glass rod that has been weighed with the beaker. Let stand until thoroughly settled, decanting into a 32-oz. beaker. Repeat washing with benzine until the sample is free from oil. (It is best to wash four or five times, the number, of course, depending upon the character of the pigment and how far it settles in the beaker.) Finally add any pigment that may have settled out in the large beaker due to decanting too soon or to accident while doing so. Dry in an oven until free from benzine. When dry, weigh the rod with the contents of the beaker, then subtract from this result the weight of the beaker and rod, and get grams pigment in 25 c.c. of paint, and from this calculating the pounds of dry pigment per 100 gallons paint. If it is desired the solution containing the oil may be evaporated to dryness and

the weight of the oil determined, in which case carbon-disulphide free from sulphur is best used as a solvent and the vapor condensed during evaporation. The washed sample may now be taken for analysis, after being thoroughly mixed and pulverized.

Determination of Water, "Turps," and Benzine. —The apparatus used is represented below. It



consists of a copper retort A, of about 200 c.c. capacity, detachable at D to admit of filling and subsequent cleaning. G is a small opening for admission of coal gas. (This may be dispensed with, but when used it should be freed from moisture by passing through $CaCl_2$.) The copper tube leading from the retort is connected at B to the glass condenser C. A copper oven, open at the bottom excepting for a covering of copper gauze, is fitted over the apparatus as shown. It contains

a thermometer T, and is heated by a Bunsen burner E. H is a vessel containing cold water, in which is immersed a 10 c.c. cylinder graduated in $\frac{1}{10}$ c.c. for collecting the distillate.

PROCESS. — Measure off accurately in a graduate 100 c.c. of the thoroughly stirred sample and pour it into the retort. Let drain thoroughly. A small amount will still remain in the cylinder and should be washed down with 50 c.c. benzine accurately measured. By subtracting the amount of benzine used from the resultant liquid in the measuring cylinder the amount of paint that remained may be estimated, and from this the amount of paint used in the retort. Now connect the apparatus, placing a cork in G or, better, connecting with a stream of well dried coal gas. Heat the oven at 110° C. to 120° C., taking care that the temperature does not rise above this, until no more distillate comes over. If any water is present it will be found in the lower layer, while any benzine will be found on top. In case the cylinder becomes full before all the distillate is collected, read off the respective volumes of each and replace it by another 10 c.c. cylinder, collecting the remainder, and adding to the previous amount. Now increase the temperature gradually to 175° C., collecting any distillate that may come over, and keep at that temperature until no further distillate appears. This is read off and recorded as "turps." The c.c. water, benzine, and "turps" thus obtained are equivalent to

the same number of gallons in the number of gallons of paint equal to the c.c. paint taken. Calculate to gallons, water, "turps," and benzine in 100 gallons of paint.

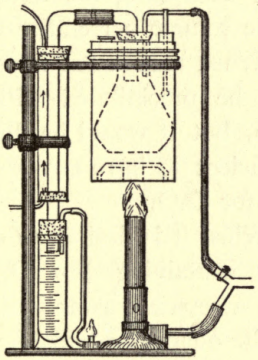
The above results will always be found low. In case turpentine is present in considerable quantity the vapor from it will drive off practically all the water and benzine, but not all of the turpentine itself will distil over. If desired the water, "turps" and benzine may be distilled together at the high temperature (175° C. to 185° C.). The volume of water may then be read off and partly separated from the "turps" and benzine by a glass-stoppered separatory funnel and finally completely removed by shaking the residue in the funnel with well dried calcium chloride. The ratio of "turps" and benzine may now be determined as described under Turpentine in Chapter V.

The following apparatus and method is recommended by George H. Ellis, who has used it satisfactorily for several years.

The apparatus consists of a copper cylinder detachable at the top and with an opening at the bottom covered with copper gauze. This is clamped to an upright support and contains an Erlingmyer flask supported from the top, fitted with an entrance tube for gas and connected with the condenser. A thermometer is inserted in the copper cylinder. The gas passing through the apparatus is allowed to pass out of the graduate and is then

burned. Its flow is regulated by means of a small stopcock in the glass Y.

Twenty-five to fifty grams of the paint or varnish are weighed out and mixed with sufficient thoroughly dried sublimed lead to make a dry powder. This is placed in the flask by means of a funnel made from glazed paper, the apparatus connected, and the distillation proceeded with as in the former



method. By this means the volatile portion seems to distil more readily, and after completing the determination the flask is more easily cleaned. The graduate is weighed, and when all water and benzine have distilled over, the graduate and contents are weighed and the increase in weight equals water and benzine. The weight of water in grams is equal to the c.c. present, and the difference equals benzine.

The temperature is now increased to 175° C., all turpentine collected and determined by the further

increase in weight. From the weight of paint taken, the percentage by weight of water, turpentine, and benzine can be readily calculated.

It will be observed that this method gives the percentage thinners by weight and not by volume, as does the former method. In the author's opinion this is not so convenient and it requires more time to weigh the sample than to measure it. If desired, the method of measuring the liquid can be used instead and the volume percentage thus obtained.

Note 1. When manganese is present in tinted paints it will be precipitated with zinc by the methods given, but it would hardly be present in quantities sufficient to have any appreciable effect on the results for ZnO.

Note 2. When it is desired to obtain Cr_2O_3 in a tinted paint containing $PbCrO_4$, it should be determined on a separate sample of 10 to 20 gms. according to the quantity present. Digest with an excess of dilute HNO_3 and alcohol until all the chromate is dissolved and reduced to the chromic salt. Add sufficient H_2SO_4 to precipitate all lead present, separate in the usual manner, precipitate Cr in the filtrate with NH_4Cl and NH_4OH, and separate from any iron present by I. II.

CHAPTER IV

THE MATCHING OF SAMPLES

Dry Colors. — In order to properly match samples of dry colors, and supply materials according to the sample, a very large line of colors is necessary with the proper facilities for mixing. Colors of the same shade should be at hand containing various percentages of adulteration, in addition to the pure colors. The exact percentage of impurities, and the kind, should be known in all cases. To make a special color by precipitation for every sample submitted is out of the question, and can only be attempted where a large contract is to be filled.

The chemist should get approximately the percentage of the materials needed to closely match the sample in shade and composition. A small mix should then be made and ground on sample mill. If the shade is not correct the formula is varied and different mixes made until the desired shade is produced, always varying the materials in such a way as to keep the percentage adulteration and the kind of adulterating materials the same. Adding the straight adulteration to reduce the material to the same grade as the sample should be avoided whenever possible. A strength test is then made between

the material thus produced and the sample, in order to check results. The strength of pure greens, yellows, and blues of different makes will, in most cases, be found to be the same. A c.p. chrome yellow is now on the market, however, which is fully 40 per cent stronger than the average pure chrome yellow, and it is obvious that a green made from this material would also have extra strength. A discrepancy would then be shown in this case between the analysis and strength test, and under such conditions the color should be matched according to strength. Pure blues will be found to vary but little in strength (*i.e.*, Chinese from Chinese, and Prussian from Prussian — Chinese is a much stronger color than Prussian) and are best matched by strength alone, the shade in oil and the tint always being taken into consideration.

Where a dry color is to be used for tinting this fact should be taken into consideration and the tint matched. It is not usually necessary to match the sample dry as well as in oil, unless the color is to be used as a distemper color.

1. a. VERMILIONS, EOSINE AND SCARLET. — Owing to the wide variation in the strength of red leads and orange minerals the strength of the resultant vermilions also varies through wide limits, and in matching a vermilion, whether dry or in oil, this fact must always be taken into consideration. The shade in oil will generally give some idea of the grade of the lead in the vermilion, but not

always. The bulk is also of great importance. The first thing to do in matching a sample of vermilion is to match the shade in oil. Then make a small sample with the same percentage Pb_3O_4 and adulteration as the sample to be matched, and try the strength. To be a proper match the strength should be the same. If not, changes must be made until this is accomplished. It sometimes occurs that the color cannot be matched in shade and composition as found by analysis and the same strength obtained. In this case the adulteration should be varied from that shown by analysis until the desired strength is produced. To properly match dry vermilions a large line of vermilions of different grades and purity is necessary, and without these satisfactory results cannot be obtained.

1. b. PERMANENT REDS, DRY AND PASTE. — Permanent reds may usually be matched from the analysis, but where they contain red lead this cannot easily be done. If the chemist has on hand permanent reds containing known percentages of dye, red lead, orange minerals, etc., he can match them in much the same manner as in other vermilions, seeking that combination which will give him the proper shade in oil and strength, and conform to the analysis of the sample. Complications arise, however, owing to the difference in character and properties between the coloring matter produced by the addition of diazotized para nitranaline and beta naphthol and the darker shade produced by the

additional presence of mono-sulphonic acid. The latter will show the same as the former in analysis, but is stronger and has a bluer undertone.

Whenever possible it will be found advisable and more economical to match samples of permanent red in oil containing orange mineral, by using the pure toner in the proportion found by analysis, grinding with it the orange mineral and other materials found present. If the orange mineral used has the proper strength and the toner is of the proper character the resultant shade should have the same depth of color as the sample. Otherwise different grades of orange mineral should be tried until one is found which gives the proper results.

2. **Untinted Colors in Oil, Japan, and Varnish.** — It is first necessary to get some idea of the vehicle in which the material is ground. To determine the grade of the vehicle used by chemical tests is impossible, but by simple tests a fairly accurate idea may be gained. Only wide experience, however, will make one competent to do this. The colors should be spread out thin on glass, and its time of drying noted, also the way in which it dries; its odor, hardness, etc. The manner in which japan and varnish colors spread is important.

The grade of pigment must also be taken into consideration, as it is very unusual to grind cheap colors in expensive vehicles, and vice versa. Corn, cottonseed, and mineral oils when present in any considerable quantities can often be detected by

the odor. When a deodorizer such as oil of myrbane is present one can always be certain that some adulterating oil is present in large quantities. Pastes are often ground in a mixture of benzine and oil, in which case the paste will dry flat without the smoothness and hardness of a japan color, and the benzine can be determined by drying a weighed portion of the sample at 100° to 110° to constant weight. The chemist should try pastes made up with different vehicles at hand, note their properties and try different mixtures until he becomes thoroughly acquainted with the action of all vehicles at hand. With practice mixtures of oil and japan, oil and varnish, japan and varnish, etc., can be readily distinguished. The paste which is to be furnished should be so made as to be like the sample in drying, gloss, odor, and all other physical properties. The proper matching of the vehicle is as important as the proper matching of the pigment, and should be done with the greatest of care.

The colors should be matched on glass ground in the proper vehicle, using pure colors whenever possible, adding the adulteration in the proportion found by analysis. In the case of japan colors the sample thus made and the sample to be matched should be allowed to dry thoroughly side by side on glass, and then varnished over to be certain that the shade is correct. It will be found cheaper to use the c.p. colors and add the adulteration when mixing than to use colors which have been adul-

terated in making; but oftentimes the proper shade cannot be produced by the former method, owing to the fact that the adulteration when mixed will flat more than when made in the color. Match vermilion pastes as given under Vermilion Dry Colors.

3. **White and Tinted Pastes.** — Take the zinc, sulphate of lead, and white lead, whiting, etc., in the proportions found in the sample, and tint to shade with pure colors whenever possible. In case impure tinters are used, such as umbers, oxides, etc., the amount of foreign matter in these must be calculated and a corresponding amount subtracted from the adulteration to be added. On this account it is imperative that the percentage purity of all stock materials be known.

4. **White and Tinted Paints.** — Make up paste as in 3 to match shade of mixed paint, but make a trifle darker as the shade will become lighter on thinning. On the whole it will be found more rapid and convenient to grind together in proper proportions all materials found by analysis, excepting tinters which are added afterwards in liquid form to the proper shade. In either case any adulteration in the tinters must be taken into consideration, as in 3. It is best to make up about a quart sample first. Reduce pounds of dry pigment found per 100 gallons to ounce per quart, and gallons water, benzine, and turps to fractions gallons per quart. Now weigh out such a proportion of paste as will give the proper ounces dry

pigment per quart as found, add to this the proper amount of water, turps, and benzine (also enough drier to make paint dry as does sample, deducing thinners in this from benzine and turps to be added) as found, and make up to volume with oil, or in case oil has been determined direct, add first in the proportion found. In case no water is present the resultant paint should have the same consistency as the sample.

If water is present it may be too thick or too thin, showing that there was too much or too little alkali in the water used. In this case the strength of the water solution must be varied until the proper consistency is obtained.

The proper oil to use offers a very difficult problem. Some idea of it may be gained by noting the way the paint dries, and by extracting some of the oil with chloroform or ether, and examining according to Chapter V. This will give but little satisfaction in many cases, however, owing to the presence of drier, etc.; but here, as in paste goods, it will almost invariably be found that paints containing cheap pigments will contain cheap oil. Usually a considerable amount of corn or cottonseed oil is used when price permits. In second-grade paints gloss oil will often be present in considerable proportions.

In making a mixed paint where good results are desired the presence of water should best be avoided. As alkali or some other material, such as bleaching

powder, must always be added with it, a certain amount of oil is destroyed and a larger amount of soluble material formed. If gloss oil (or a drier that contains rosin) and sublimed products accompany it, the paint will thicken much more rapidly than it would otherwise do, so that after a few months it will be found to be unusable. The practice of mixing gloss oil with sublimed products (except possibly the highest grade of zinc) is dangerous at the best, and where water is used is certain to result disastrously.

5. **Yellow Ochre Tints.** — First take the proper proportions of materials as found by analysis, excepting the ochreous materials, then tint to shade with yellow ochre. If the amount of ochre required is not as great as found by analysis, make up by the addition of china clay. It will occasionally be found that since the ochre used in the sample is unusually strong, more ochre must be used in matching it than the analysis shows.

6. **Ultramarine Tints.** — As stated under the analysis of ultramarine tints, complications often arise owing to the fact that the ultramarine itself contains materials essential to its composition that are often used for adulteration. Under ordinary circumstances the ultramarine may be approximated from the per cent of Al_2O_3 and SiO_2 present, but in the case of free SiO_2 and silicates the analysis becomes complicated and the following method should be used in matching: —

Take the white body pigments (*i.e.*, zinc and lead compounds), together with any barytes, whiting, etc., in the proportion found by analysis, and tint to shade with ultramarine. In case this does not make a total of 100, add adulteration (silica or china clay) until such is the case.

CHAPTER V

PAINT VEHICLES

I. OILS

The oils used to any great extent in the manufacture of paints are linseed (raw, boiled, and bleached), cottonseed, corn, and the so-called mineral and rosin oils. China wood oil, although now used extensively in the manufacture of varnish, has made no headway in paints, owing to the fact that without proper treatment it will dry "flat" or dead and cause the same result when present in any appreciable quantity in other oils or vehicles.

Menhaden oil is restricted by its fishy odor, which has long kept it from taking its proper important place in paint manufacturing. It has been used to some small extent for painting where much friction is improbable, and the author is informed on the best of authority that it has shown itself equal or superior to linseed in wearing properties.

The problem of oil analysis is one which has been worked on extensively, but only with a limited degree of success. The author is of the opinion that a vast number of tests suggested are worthless. It would seem that the many discrepancies among authorities as to the characteristics of different oils can only be accounted for by assuming that some

have worked with impure oils or with oils in different conditions. For instance, results obtained by experimenting on raw, bleached, and fatty linseed would be very different, although the oil may be correctly called linseed oil in each case. Owing to the unsettled nature of our present analytical knowledge of oils the chemist should be careful in accepting tests without first determining their reliability by experiments performed on samples of known purity. The few tests given below are carefully selected and are among the most reliable in use, but nevertheless should be checked against samples of known content if used for the first time.

Special Tests

1. **Iodine Number.** (*a*) **Hübl Method.**—0.2 gms. oil or 0.4 gms. solid fat are dissolved in 10 c.c. chloroform in a stoppered flask, and 20 c.c. iodine solution added. This is made by dissolving 25 gms. I in ½ liter alcohol, and 30 gms. mercuric chloride in ½ liter of alcohol, the two solutions mixed, allowed to stand twelve hours, and then standardized with n/10 $Na_2S_2O_3$ (see C. V.). After the mixture of iodine and oil has stood for eight hours, transfer to a beaker, rinse flask with KI solution, add 150 c.c. H_2O, and if the solution is not clear add more KI until such is the case. Determine the excess of I by n/10 $Na_2S_2O_3$ as in C. V., and calculate I absorbed by 100 gms. oil or fat. For interpretation of results see Table IV, Appendix.

The iodine solution changes strength very rapidly. It should always be restandardized immediately before using and an additional amount added to the oil solution to make up for the loss in strength. The iodine must always be kept in considerable excess or results will be obtained which are entirely unreliable. Keep the solution tightly stoppered in a cool, dark place.

(*b*) **Wijs Method.**—The variation of this method, known as the Wijs method, gives an iodine solution which is much more stable than the Hübl solution and acts with much greater rapidity. Thirteen gms. of pure iodine are dissolved in a liter of 99 per cent c.p. acetic acid and the strength determined with standard sodium thio-sulphate. Chlorine gas free from HCl is then passed into the solution until it oxidizes twice as much thio-sulphate. The proper ending of the chlorination may be ascertained by the change of color from dark brown to light yellow. If the gas is passed in until this just occurs the first titration may be dispensed with. The determination of the iodine number is now carried on in exactly the same manner as in the Hübl method, with the exception that the time required for absorption is greatly lessened. When small quantities of fat having a low iodine value are used the action is complete in less than five minutes, and with fats of higher values no more than ten minutes are required.

Lewkowitsch states that when c.p. 99 per cent

acid is used the solution remains permanent for two months, but varies considerably when 95 per cent acid is used.

2. **Saponification Number.**—The following, known as the Leffmann-Beam method, is highly recommended and may be used with more certainty of complete saponification than any other method now in use. When the presence of mineral oil is known in any vegetable oil the saponification number gives a very good basis for estimating it quantitatively. It also has been recommended for the quantitative estimation of rosin and rosin oil, but will be found unsatisfactory for this purpose since both of these substances, rosin in particular, take up a certain amount of alkali. Linseed, corn, cottonseed, china wood, and menhaden oil, all have practically the same saponification number, *i.e.*, require the same amount of alkali to change to a soap. They are ethereal salts of fatty acids and are decomposed by caustic soda in practically the same manner as are the salts of most metals with the formation of the soap, a sodium salt of the fatty acids present, and glycerine, a hydroxide. As petroleum products are hydrocarbons of entirely different composition and unaffected by alkali, it will be at once seen that their presence in any of the above oils will lower their saponification number, or mgms. KOH necessary to saponify 1 gram, in a direct ratio to the amount present.

GLYCERINE-SODA SOLUTION.—Add 20 c.c. of a 50

per cent solution of NaOH to 150 c.c. of pure concentrated glycerine. The soda must be as free from carbonates as possible

Method: Measure out 20 c.c. glycerine-soda solution and weigh. Make up to 250 c.c. with alcohol and titrate with decinormal oxalic acid solution made by dissolving 6.3024 gms. c.p. oxalic acid in 1 liter of water. This may be checked against a standard alkali solution to make certain that it is correct.

The strength of the glycerine-soda solution having been established in grams KOH per 1 gm. solution, weigh out about 25 gms. in the saponification flask. Weigh the flask containing the oil to be tested and add about 5 c.c. to the glycerine-soda solution, and again weigh the flask containing the oil, obtaining the weight of sample used by difference. The saponification flask is now heated until complete saponification takes place, care being taken that the heat is not sufficient to decompose the glycerine, which can be observed by the odor of acroleïn. Complete saponification should take place in less than five minutes (unless unsaponifiable materials are present) as evidenced by the mixture becoming perfectly clear. Dissolve the soap in alcohol. Make up to 250 c.c. and titrate excess of KOH with oxalic acid. Subtract this from total KOH used in the glycerine-soda solution taken, and calculate mgms. KOH necessary to saponify 1 gm. oil. (See Table IV, Appendix.)

3. **Flash Test.**—This test may be performed in any flash test apparatus at the operator's command, and will be found very valuable in establishing the purity of linseed oil. It will be found safer to test oils of known purity in whatever apparatus is used, and keep the results thus obtained as a check rather than to rely on tables given by others. In making the flash test it should always be the aim of the operator to keep the conditions as nearly constant in all cases as possible. The temperature should be increased about 5° C. to 10° C. per minute, the test flame being applied at each 5° rise. The heat must not be concentrated over too small an area of the bottom of the cup, as this may give rise to bubbling of the oil, which will cause small particles of it to be thrown from the surface where the open tester is used. These particles will burn on coming in contact with the test flame and may be mistaken for the flashing point. The test flame should be very small and always applied in the same place; same quantity of oil should always be used, and draughts avoided. The flashing point will be noted by the appearance of a slight bluish flame, accompanied by a faint explosion when the test flame is applied. In the case of the open tester this flame appears around the sides of the container.

The following results were obtained by the author with an apparatus consisting of a copper cup heated by a Chaddock burner, which will be found very satisfactory.

OIL	FLASHING POINT °C.
Linseed, raw	295°
Linseed, boiled (fire boiled with Mn and Pb driers)	275°
China Wood	280°
Corn	245°–249°
Crude Cottonseed	238°
Summer Y Cottonseed	360°
Winter Strained Menhaden Dark	252°
Rosin, light body	80°
Rosin, medium body	100°
Rosin, heavy body	140°
Penn. white neutral sp. gr. .857	156°
5% neutral sp. gr. .857 / 95% raw oil	225°

The flashing point of vegetable oils seems to vary considerably on aging. Before declaring a sample of linseed oil adulterated because of a low flashing point it should be remembered that very small quantities of benzine, kerosene, and turpentine will decrease the flashing point many degrees, and it must be decided whether the adulteration is present in large enough quantities to show intentional adulteration, or whether it is due to the use of unclean barrels which may have contained small amounts of any of these three substances.

4. **Sulphuric Acid Test.** — The bleaching of raw

oil by sulphuric acid and steam is one of the most widely used methods of preparing bleached oils. Crude cotton, fish, and rosin oils are darkened by sulphuric, and the author has adapted the following method to determine their presence in linseed:—

To 100 c.c. sample oil add ½ c.c. H_2SO_4, 66° B. Stir thoroughly, finally removing the gummy matter that collects on the end of the stirring rod. A sample of raw linseed of known purity should be treated in like manner. After settling thoroughly (over night or longer) the pure linseed will be found to be about the same in color as before treatment (boiling with steam necessary to bleach), while an oil containing 5 per cent rosin oil, 10 per cent crude cotton or menhaden, and over 20 per cent corn and refined cotton, will be considerably darker, increasing with the amount of impurities present. The addition of sulphuric acid makes the odor of rosin oil very noticeable when present in quantities as small as 5 per cent, while another peculiarity when 15 to 20 per cent or over of any adulteration is present is the very marked decrease in the amount of gummy matter collecting on the end of the stirring rod.

5. **Taste and Odor.** — The taste of an oil is often of great value in determining what impurities may be present; also the odor developed on heating. With practice, the presence of foreign oils in raw linseed should be identified by taste when present in the following amounts:—

15%–20% corn.
15%–20% refined cottonseed.
10%–15% crude cottonseed.
5%–10% menhaden, crude and refined.
5%–rosin oil.
5%–neutral oil.

6. **Test for Rosin.** — The presence of rosin in quantities as small as 5 per cent can be determined by the Liebermann–Storch reaction. This may be performed by placing two drops of the oil to be tested on a watch glass placed on a white paper. Two or three drops of acid acetic anhydride are then added, the mixture is stirred and a drop of concentrated sulphuric acid added, when, in the presence of rosin, a purple coloration will form on the edge of the mixture, and quickly disappear. This test should be applied to pure linseed oil to which known amounts of rosin have been added so as to familiarize the operator with the reaction. The only other material (a constituent of some animal fats) which produces this color will never be found in paint oils, and the appearance of this coloration can be relied upon as showing the presence of rosin.

Regardless of many statements to the contrary this method as above performed, or any variation of it, cannot be used for the detection of rosin oil or rosin spirits when a reddish coloration is produced, which is not at all characteristic.

7. **Halphen's Test for Cottonseed Oil.** — 5 c.c. oil

to be tested are placed in a test tube together with 5 c.c. amyl acetate and 5 c.c. carbon disulphide containing 2 per cent of sulphur in solution. The tube is heated for fifteen minutes in a parafine bath at 110° C. The presence of cottonseed oil is indicated by the appearance of a pink color, becoming more intense with the amount present. Cottonseed oil which has been heated to 245° C.–265° C. will not respond to this test, but such treatment would hardly be given an oil used to adulterate linseed.

(A) Drying Oils

Linseed Oil, Raw. — Per cent oil in seed, 38–40. Constants: Sp. gr. at 15° C., .9315–.935. Flashing point, 295° C. Iodine number, 172. Saponification number, 192.

Linseed oil is obtained from the seed of the flax plant by extraction or subjection to hydraulic pressure. The cold pressed is thicker and lighter in color and has a higher iodine and saponification number than has the warm pressed whose constants are given above. Warm pressed oil is golden yellow, sometimes slightly greenish in color, becoming very light colored when heated rapidly to its spontaneous flashing point. On further heating it takes up oxygen very rapidly, becoming thick and darker, until finally it becomes gummy.

Probable Adulterants. Rosin oil, rosin, mineral oils, very rarely corn, cottonseed, and menhaden oils. As regards the latter named oils their pres-

ence in linseed will only occur when the difference in cost is considerable. It should be borne in mind that when the cost of linseed is as much as five cents a gallon advanced over the cost of these oils, adulteration with them offers but little advantage to the crusher, as they will then cost him about as much as linseed. A shortage of seed with oil contracts to fill might lead to its being done in rare instances.

The presence of rosin oil and mineral oil will be shown by the flash test. The sulphuric test may give a clue to the one present, and the saponification number the amount. Rosin should be tested for by method 6. The iodine number may very often be used to advantage, but it should be remembered that "foots" in the oil are very liable to lower the iodine absorption, and an oil to be tested should be clarified if possible. "Foots" can hardly be considered adulteration, but offers grounds for complaint against an oil, causing a lowering of the saponification as well as of the iodine number and interfering somewhat with drying. Impure seed often imparts a foreign taste to the oil.

Boiled Oil. — Constants: Sp. gr. 15° C., .936–.938. Iodine, 165–175. Saponification, 190.

This oil is usually prepared by heating raw oil to about 250° F. and adding the drier (which has been previously prepared by heating raw oil to a temperature of 450° to 500° F., with a mixture of lead and manganese compounds until the materials are dissolved), then keeping the oil at that tempera-

ture for several hours. So-called "bunge" boiled oils are made by adding the drier direct to the raw oil without heat, and where the drier is made from pure linseed are practically impossible to detect. As is often the case, however, the drier added will contain naphtha, mineral oil, or rosin oil, which will at once be shown by the flash test, and such an oil must be pronounced adulterated.

A properly boiled oil should dry in eight to twelve hours, but the fact that it does not cannot be taken as showing adulteration, but may be due to the addition of too little drier.

Boiled oil can be tested for purity in the same manner as raw linseed, but not with the same certainty of results. The dark color renders the sulphuric test of little value excepting when considerable adulteration is present, and also obscures the Halphen reaction if cottonseed is present in small quantities. The presence of rosin may be detected by the Lieberman-Storch reaction. Rosinates used in boiled oil as a drier should not be present in quantities sufficient to give this reaction. The author is accustomed to test boiled oil in which rosin is found by mixing to a paste with litharge and allowing to stand twenty-four to forty-eight hours. Rosin present in the drier as rosinate should not be in sufficient quantities to cause the mixture to become thick or perhaps hard. When such is the case the oil must at once be condemned. It will always be found safer not to use a boiled oil which

gives any test for rosin. Rosin and mineral oils will be shown by the flash test, and the amount can be approximated by determining the iodine or saponification number.

Bleached Oil. — Constants: Sp. gr. at 15° C., 930–938. Iodine number, 170–180. Saponification, 192.

This oil may be prepared by treatment of raw oil with sulphuric acid and steam; a mixture of sulphuric acid, chromic acid, and steam; by heating to a high temperature and subsequently chilling; by heating to 110° C. and forcing air and steam through it; and by several other methods involving similar operations. The acid bleached is generally used for paint manufacturing, while the fire bleached is sometimes used in varnish making as it discolors less when heated than the raw or acid bleached oils.

The constants for bleached oils vary with the method employed in bleaching, the air blown having its specific gravity increased and iodine number diminished over value given above, owing to the absorption of oxygen. The acid bleached should always be tested for sulphuric acid by boiling with water, separating and testing for sulphates with barium chloride. The presence of acid and moisture will be found to affect the oil when it is mixed with pigments, increasing the amount necessary to grind to a paste. Test for purity in same manner as raw oil. A varnish maker's bleached oil should have an iodine number of 180 and bleach white at 325° C.

Lithographer's Oil. — This is a very thick linseed oil prepared by long boiling at a high temperature nearly approaching the spontaneous flashing point; or at a lower temperature by forcing air through it. It is used chiefly in the manufacture of printing inks, but occasionally in paints, being added to fillers, japans, or varnish goods. The specific gravity and iodine number vary with the thickness of the oil and are of little value in determining purity. Rosin, rosin oil, and light mineral oil can be readily detected by the usual tests. Mineral oil of high flashing point could be detected only by determining the saponification number. As lithographer's oil has a decided bloom, this must not be taken as showing the presence of mineral oil.

China Wood Oil. — China wood oil is obtained by cold pressure from the seeds of the tung tree, a plant which grows very extensively on the banks of the Yangtze River in China. It has recently come into extensive use in the manufacture of varnish. Its peculiar property of drying flat, with a surface somewhat resembling ground glass, has up to the present time prevented its use to any extent in the manufacture of paints. Either alone or with pigments it dries with a dead surface, and even when used in a small proportion with other oils and varnish it tends to cause flatting and sometimes crinkling. The former property has been utilized to produce flatting varnishes without necessitating the use of wax.

In addition to the above property China wood oil has other peculiarities which render it vastly different from all other drying oils. The odor is very characteristic and stubbornly resists destruction, regardless of the manner in which the oil is treated. This admits of its identification when present in but small proportions in varnishes, etc., regardless of other constituents. Another very interesting property is the instant change into a jelly-like substance when heated to about 285° C. to 300° C. The material this produces is insoluble in all ordinary solvents and cannot be melted by further heating.

The properties of this oil that have led to its extensive use in the manufacture of varnish are several. The oil may be heated without discoloration; it can be treated so as to remove the tendency to flat, and then produces varnishes with a very fine gloss; it has the property of drying hard but tough, and when used with rosin will produce a more elastic varnish than will linseed oil. Its use has made possible the large number of good wearing varnishes now produced at a low cost.

In the manufacture of light driers and japans, this oil has been used to great advantage. Very powerful light driers can be produced by dissolving in it, at about 200° C., red lead and manganese rosinate with a small proportion of manganese borate added. The latter does not dissolve to any

appreciable extent, but has a tendency to keep the oil lighter in color.

The best grade of china wood oil is thicker than linseed oil, and very light in color, with the specific gravity of .944 at 15° C., and flashing point 280° C. It dries much faster than linseed and in a somewhat different manner. The drying appears to take place throughout the entire body of the oil at the same time, instead of from the top down. When heated to about 260° C. with pure manganese borate the oil is in no way discolored if pure, and even has a tendency to become lighter.

A most peculiar property of this oil is exhibited by this treatment. If 100 parts of the oil are heated to about 270° C. with 8 parts white manganese borate until a scum begins to form on top, and then mixed with as much as 700 parts of benzine and allowed to stand so as to be slightly accessible to air for a few days, the mixture will be found to consist of a thick water-white liquid, having much the appearance of gelatine. If allowed to remain longer it will be converted into a white translucent solid. Before the latter action has taken place, it may be mixed with oil or varnish, which if added in quantities as great or greater than equal parts will tend to stop further action. The same action takes place if less borate is used, but more slowly. This is also the case when turpentine is substituted in place of benzine. The liquid thus produced differs also from the benzine liquid in being more

like varnish in appearance than like gelatine, *i.e.*, not being so "short."

It seems more than probable that in the future this oil will be used extensively in the manufacture of paints. At present no method is available to remove the property of flatting without the use of more heat than is generally at the command of the paint-maker.

Menhaden Oil. — Sp. gr., .927–.932. Iodine number, 156–160. Saponification number, 190–192.

This oil is prepared from the menhaden fish by steaming and subjecting to pressure. It varies from the very dark, strong smelling crude to the very white winter bleached. Caustic soda is used in refining. By proper manipulation all grades can be completely deodorized.

Menhaden oil oxidizes readily in the air, drying much faster than linseed but never gets very hard. It wears very well and on the whole is the most satisfactory substitute for linseed that is produced. Its odor has prevented its use in paints, but it seems probable that this objection will be overcome, and when this is accomplished it should entirely displace corn and cottonseed oil for use in prepared paints.

Probable adulterants. Rosin, rosin oil, mineral oil. Test as in raw oil.

(B) Semi-Drying Oils

Corn Oil. — Constants: Sp. gr., .920–.924. Iodine

number, 115. Flashing Point, 245° C.–249° C. Saponification number, 192.

Corn oil is prepared from the germ of the corn separated during the manufacture of starch. It is light in color and has a very characteristic taste and odor resembling corn. Taste and odor become noticeable even when mixed in small quantities with linseed oil.

By the addition of a large amount of drier corn oil may be made to dry after prolonged exposure to the air. When used with 50 per cent or more of linseed oil and the necessary amount of drier it dries fairly well, but the mixture does not seem to wear as well as pure linseed when exposed to the action of the weather.

Probable adulterants. Rosin, rosin oil, mineral oil. Test as in raw oil.

Cottonseed Oil. — Constants: Sp. gr., .922–.9235. Iodine number, 106–110. Saponification number, 193.

Cottonseed oil is obtained by subjecting the cottonseed to hydraulic pressure. The crude pressed oil is dark red in color, often with a disagreeable odor. It is purified by alkali, yielding a light, pleasant tasting oil. On chilling, large quantities of stearine settle out, leaving the winter white oil.

Cottonseed oil does not dry as well as corn oil, but otherwise behaves very much like it in paint. When a large amount is present the paint will freeze in very cold weather, owing to the fact that

crude cotton and summer yellow begin to solidify at about o° C.

Probable adulterants. Rosin, rosin oil and mineral oil. Test as in raw oil.

(C) Non-Drying Oils

Rosin Oil, Mineral Oil (not true oils). — These materials cannot properly be classed as paint vehicles, and have no standing in a reputable paint factory. They can be used to some advantage in shingle stains when the object is to leave a greasy surface to shed rain, also in small quantities in cheap putty. On the whole, cheap as they are, they are not worth their cost in paints.

Rosin oil may be found adulterated with mineral oil, but mineral oil will never be found adulterated.

II. VARNISHES, JAPANS, AND DRIERS

Knowledge of their physical characteristics and not the composition of these materials is what is desired by the paint chemist. Samples are generally submitted to be substituted for those in use or for some special work. In the former case they should be tested against the stock goods; in the latter, with the object in view for which they are to be used.

(*a*) **Driers, Prepared.** — A properly prepared drier is made by dissolving manganese and lead compounds in hot linseed or some other vegetable oil and thinning with turpentine or benzine. A drier

containing much free rosin or rosin oil should not be used, as it may result disastrously when used with sublimed products or red lead, and under all conditions will injure the life of the paint. The presence of rosinates or rosin in quantities so small as to withstand the litharge test can be used with safety.

LITHARGE TEST. — Mix the drier to a semi-paste with litharge and observe the length of time before hardening. The best driers will remain for three to four days without showing any thickening.

Note. As different brands of litharge and those containing different amounts of moisture, will cause a great variation in time of thickening with driers, etc., tests should always be made with the same material which has been previously well dried. This applies to varnishes and Japans as well. (See Oil, Paint and Drug Reporter, issue Sept. 22, 1902.)

Test drying power on raw oil, using various proportions of drier.

Color and body (when latter is not due to rosin, rosin oil, or heavy mineral oil) are important features.

The amount of benzine may be determined in supposed turpentine driers by method given under turpentine. Other conditions being the same, the drier which stands the longest with litharge without hardening, has the strongest drying power, lightest color and heaviest body, has the best value.

As thinners should also be taken into consideration it will be found very difficult to pick the best drier from a number of samples without considerable experience.

Note. The manner in which the drier dries the oil, and not the drying of the drier itself, as so many appear to think, is the important feature in this respect. The manner in which the drier dries alone will not give the slightest indication of how it will dry oil.

(*b*) **Varnishes.** — Varnishes should always be tested with a view to their use. The important features in a varnish are body, color, drying, gloss, working and wearing properties. Where a varnish is to be used for outside work it should always be tested by exposure to the weather, best on well-oiled hardwood. Its condition should be noted at frequent intervals, especially after rains.

The varnish should be flowed out on glass and its drying noted, also hardness and toughness after drying several days. Color is very important where the varnish is to be used with light shades. The gloss should be tested by mixing with the proper proportions of pigment and brushing out, at the same time noting how it flows and whether or not it gives a smooth surface.

Body is also of importance, and where the varnish is to be used with red oxide of lead vermilions it should always be tested for time of thickening with litharge, that varnish being the safest to use which

stands the longest with litharge without thickening. It is always advisable to have a large number of varnish samples at hand, all of whose properties are known, so that when one having certain characteristics is desired it may be obtained without delay.

(*c*) **Japan, Grinding.** — In testing grinding japan the use to which it is to be put should always be kept in view. Its body, color, drying, manner in which it grinds, and amount required to grind any material to a paste, are all important features. When ground with pigment and rubbed out on glass it should dry flat on top, but should not appear flat when viewed through the glass, as this indicates deficiency in body. It should dry hard in eight to ten hours, should not contain naphtha, and the presence of rosin in any quantities should be avoided.

When a japan is to be used for grinding red oxide of lead vermilions great care must be taken in its selection. A japan should not be used that will harden with litharge in less than forty-eight hours, and even this can only be safely used with the highest grade of orange mineral vermilions if they are to be kept in stock for any length of time. Vermilions in japan and varnish should only be made up as needed.

The author very strongly advises that when satisfactory grinding japans and varnishes are being used, great caution be observed in changing, doing so only after practical experiments extending over a considerable space of time.

(*d*) **Gloss Oil.** — This material is made by melting rosin with a small amount of lime and thinning with benzine or sometimes turpentine. It dries very quickly with a hard brittle surface and high gloss. On exposure to the atmosphere it is soon destroyed and can never be used alone with satisfactory results. In making very cheap paints where quick drying is of more importance than wearing properties, such as barrel paint, it may be used. When used with linseed oil it gives fair results when not present in large quantities, but its use should always be restricted to second-grade paints and used very cautiously even there. It will be found to greatly retard drying when mixed with linseed.

III. THINNERS

Under this head may be classed turpentine, benzine, rosin spirits, and benzole, the first two being the principal materials used, and the last two being found chiefly in turpentine substitutes. Turpentine manufactured by the direct distillation of pine waste is also being placed on the market. This varies somewhat in composition from pure spirits of turpentine and cannot be rightly sold as such.

Thinners in oil paints are detrimental to the life of the paint if not properly used, and should best be avoided. Owing to the fact that their presence renders the application of paint much easier, mak-

ing it less laborious to brush out, their use has become wide-spread and abused. The tendency has been to reduce the amount of oil below that required to give the paint its proper life, and to greatly increase the amount of thinners, especially with benzine, owing to its cost. This will be found to be one of the chief causes for the many unsatisfactory mixed paints now on the market.

I. **Turpentine.** — Constants: Sp. gr. 15.5° C., .862–.870. Boiling point, 156° C.–158° C. Flashing point, 36° C. (Able's Instrument).

Turpentine is manufactured by distilling pine resin in copper stills. The temperature must be carefully regulated in order to obtain the best grade of rosin which remains behind in the still. The resin from the first season's tapping produces the finest quality of rosin, *i.e.*, water white and window glass, the remaining grades varying from M to the black A.

Pure turpentine has the constants as given above, is colorless, and when spread out over a large surface evaporates without leaving any noticeable residue.

Turpentine offers several distinct advantages over benzine as a thinner in paints and varnishes. First, while evaporating at ordinary temperature it will not flash, which greatly reduces the danger from fire; second, it is a better solvent for some gums; third, it is much better in vehicles used for grinding as it evaporates much slower and has

less tendency to make pastes "short"; and, lastly, has a tendency to make all paints which contain it flow out more evenly than does benzine. It has the distinct disadvantage of costing many times more, however, and of having a greater tendency to "flat" where this may not be desired. This is increased by the fact that more of it than of benzine is required to reduce a paint to the desired consistency, owing to its greater body. Its so-called drying properties lie in the fact that when added to a paint less oil is used, the body is diminished, the paint spreads over a greater area, naturally reducing the thickness of the coat, resulting in faster drying. In this case it offers no advantage over benzine, which will produce these same results.

The Quantitative Estimation of Adulteration in Turpentine

Sulphuric Acid Number.—The following method by the author, while not giving absolute results in all cases, will be found to be very accurate for the vast majority. This test should be first employed, leaving all qualitative tests until later, as this alone may establish the purity of the sample and save unnecessary work.

Apparatus and materials: Sample turpentine of known purity, 66° B. sulphuric acid, neutral oil, 50 c.c., burette, 50 c.c. and 10 c.c. pipettes, 6-ounce beaker packed in asbestos fibre, plaster paris mold,

or any suitable material for retaining heat, thermometer 0°–100° C., finely calibrated.

The operation, which should always be made with the same materials and apparatus, is proceeded with as follows:—

50 c.c. neutral oil are accurately measured in the pipette and transferred to beaker, temperature noted, and 20 c.c. 66° B. sulphuric acid (which should be of same temperature as oil) added slowly from the burette, the time being of no great importance so long as it be slow enough to allow the acid to run down without remaining on the sides of the burette. Now stir rapidly to maximum constant temperature. The rise will vary from 0° to 10° C., depending upon the grade of neutral oil used. This rise is noted and kept for future reference. It is advisable not to use a neutral oil giving a rise of over 2° C.

50 c.c. neutral oil are now measured as before, 10 c.c. pure turpentine added, the temperature noted, 20 c.c. sulphuric added, and the maximum rise in temperature observed after stirring thoroughly. (The accuracy of the results depends largely on stirring correctly.) This will, of course, vary with the apparatus used, the strength of the acid, and the specific heat of the mineral oil. On this account it is impossible to calculate the "specific temperature reaction" as in the Maumené test, but each operator must determine his own factor with the materials used.

The rise in temperature due to the neutral oil is

now subtracted from that due to the turpentine present. It will now be found that if 10 c.c. benzine be substituted for the 10 c.c. turpentine, the rise in temperature will be the same as with the neutral oil (or a trifle less, owing to the fact that more liquid is present). The increase in temperature then due to the benzine is 0°, and from these observations it will be seen how the percentage of turpentine in a mixture of turpentine and benzine can be readily calculated, the benzine being obtained by difference.

The author gives below some of the results obtained by himself: —

No. I.

50 c.c. neutral oil
Sp. gr. .845 } Rise in temperature, 2° C.
20 c.c. H_2SO_4 66°

No. II.

50 c.c. neutral oil
10 c.c. pure "turps"
20 c.c. H_2SO_4

1. Rise in temperature 54° C.
2. Rise in temperature 53½°C.
3. Rise in temperature 54½° C.

Average 54°

No. III.

50 c.c. neutral oil
10 c.c. benzine } Rise in temperature = 2° C.
20 c.c. H_2SO_4

Therefore, in any mixture of turpentine and benzine the rise in temperature—2° C. × 1.923 gives the

percentage turpentine present with the author's materials and apparatus.

No. IV.

50 c.c. neutral oil
10 c.c. { 25% "turps" / 75% benzine } Rise = $14\frac{3}{4}°$ C.
20 c.c. H_2SO_4

$\therefore$ % turpentine present = $(14\frac{3}{4}° - 2° = 12\frac{3}{4}°) \times 1.923$ = 24.55%.

No. V.

50 c.c. neutral oil
10 c.c. { 50% "turps" / 50% benzine } Rise = 28° C.
20 c.c. H_2SO_4

$\therefore$ % turpentine = $(28° - 2°) \times 1.923 = 50\%$.

On the whole it has been the author's experience that with proper care the percentage turpentine can be readily obtained within one per cent of the correct value. A trial on old turpentine and distilled turpentine which have not been subjected to the action of air gives results the same as on the fresh material.

No. VI.

8 c.c. turps
7.1 c.c. benzine } 14 c.c. distilled off, a small amount of turpentine remaining behind.

The distillate was shaken to assure uniformity and 10 c.c. taken.

10 c.c. distillate
50 c.c. neutral oil } Rise in temperature = $27\frac{1}{4}$° C.
20 c.c. H_2SO_4

∴ turpentine present = (27.25—2°) × 1.923 = 48.55 % = %turpentine in 10 c.c. = 4.85 c.c. turpentine in 10 c.c., or 10 c.c. contains 5.15 c.c. benzine.

∴ 5.15 × 1.4 = 7.2 c.c. benzine in 15.1 c.c. sample.

No. VII.

Sample T damar varnish containing 25 gallons benzine per 100 gallons varnish.

30 c.c. taken and 15 c.c. distillate collected.

10 c.c. distillate
50 c.c. neutral oil } Rise in temperature = 29° C.
20 c.c. H_2SO_4

(29°—2°) × 1.923 = 51.9% turpentine.
= 5.19 c.c. turpentine in 10 c.c. dist.
= 4.81 c.c. benzine in 10 c.c. dist.
= 7.2 c.c. benzine in 15 c.c. dist., which may be assumed to contain all the benzine in 30 c.c. varnish.

∴ as determined, 100 c.c. varnish contains 24 c.c. benzine.

It will be seen that the above method may be employed to obtain the amount of benzine in varnishes, driers, etc., which are sold as pure turpentine products. It will be found impossible to distil off all of the thinners, but if turpentine is

present in any considerable quantity, and the process carried to such a point that no further distillate will come over, it may be safely assumed that all the benzine in the sample is present in the distillate, and the amount determined as above.

Kerosene gives results similar to benzine, and when shown qualitatively by remaining behind on paper after evaporation of turpentine should be determined in the same manner.

The presence of benzole and rosin spirits, which may sometimes be found in turpentine and turpentine substitutes, would complicate matters considerably. As regards benzole a sample examined by the author gave results similar to benzine and readily determined, but a mixture of benzole, benzine, and turpentine could only be approximated. In such a case the turpentine could be accurately obtained, but the benzole and benzine could only be approximated by calculation from the specific gravity, assuming the specific gravity of benzole to be the same as turpentine.

Rosin spirits will be found to still further complicate matters, as it gives a small rise in temperature with sulphuric acid. The following result was obtained on a sample of rosin spirits of known purity, specific gravity .871: —

10 c.c. rosin spirits 50 c.c. neutral oil 20 c.c. H_2SO_4	Rise in temperature 10° C., rise due to rosin spirits, 8° C.

Whether or not the rise in temperature of rosin spirits is a constant the author finds it impossible to state, owing to the difficulty found in obtaining samples. Assuming that it is, and qualitative tests show its presence, no great error would be made in calculating the amount of turpentine as in benzine, if the rosin spirits be present in small quantities. When present in any considerable quantities, the amount of turpentine can be estimated as in presence of benzine, the amount of rosin spirits obtained by difference and the per cent of turpentine recalculated, taking into account the rise due to the rosin spirits. If benzine also is present, quantitative estimations of all three would be impossible, but by determining the percentage of turpentine as if nothing but benzine were present, then calculating the percentage of benzine present by specific gravity (assuming the specific gravity of rosin spirits to be the same as turpentine), finally recalculating the turpentine, taking into consideration the rise in temperature due to the rosin spirits as determined, results may be obtained that, while they cannot be depended upon to any extent (unless the turpentine is present in very much greater amounts than is the rosin spirits) may often be found of value. The amount of rosin spirits produced is so small, however, that it is doubtful that it is in any way used to adulterate turpentine.

In testing the purity of turpentine, then, the above test should be first applied. If the proper result

is obtained no further test is necessary to establish the purity of the sample. If such is not the case adulteration is certain. As the method gives the percentage turpentine direct, the percentage adulteration is known except when complications may arise by the presence of wood turpentine and other materials mentioned above. Wood turpentine itself gives results similar to adulterated turpentine. Adulteration, however, can be established by the following table and the two articles thus distinguished from each other:

Sulphuric Acid Number.	Specific Gravity.	Flashing Point.	Boiling Point.	Evaporation on Paper.	Adulterating Material Present.
Low.	Low.	Low.	Low.	No Residue.	Benzine.
Low.	O.K.	Low.	Low.	No Residue.	Benzole.
Low.	Low.	O.K.	O.K.	Greasy Stain.	Kerosene.
Low.	O.K. or High.	Low.	Low.	Greasy Stain.	Unrefined Rosin Spirits.
Low.	O.K.	O.K.	O.K.	Little or no Residue.	Refined Rosin Spirits, or Wood Turpentine.
O.K.	O.K.	O.K.	O.K.	No Residue.	None.

A closed tester should be used to determine the flashing point. Any appreciable quantities of

benzine or benzole will cause the sample to flash at ordinary temperature, *i.e.*, about 23° C.

The specific gravity should be determined with either the Westphal balance or the specific gravity bottle in conjunction with a delicate analytical balance.

By boiling point is meant that temperature at which boiling first begins. Turpentine, consisting as it does of a mixture of several terpenes of different boiling points, has not one definite temperature at which it is completely distilled, as is the case with a single chemical compound such as water.

Wood turpentine in any quantity will be shown only by the sulphuric acid number and by any peculiarity of odor it may possess. (See also Wood Turpentine.)

The nature of the adulterating material having now been established by the above tests as well as by the odor, the calculation of the composition of the sample is taken up as given under the sulphuric acid number.

Wood Turpentine. — This article, which is manufactured by the direct distillation of pine waste, is beginning to occupy an important position as a substitute for turpentine. Samples from different manufacturers examined by the author show a considerable difference chemically from spirits of turpentine and from each other, although all have practically the same percentage composition.

These samples all appeared quite as satisfactory

to use as spirits of turpentine, as well as having the same specific gravity, nearly the same boiling point, evaporating in the same time, and not flashing at ordinary temperature. With one exception all were quite different in odor.

This difference in odor alone cannot be urged as an objection to the sale of this article under the brand of spirits of turpentine. The peculiar odor of turpentine is due to aldehyde-like products caused by the action of light and air. The presence of creosote in wood turpentine would of course be an impurity, but this should be eliminated by thorough washing with caustic soda before the final distillation, to dissolve the phenol and cresols present. As is known, the odor of ordinary turpentine varies with age and action of sunlight, and a difference in odor between turpentine prepared by two different methods can no more be urged as showing the impurity of one than can the difference in odor between acid-bleached and fire-bleached linseed oil be propounded as showing one of these products to be impure.

Aside from the odor, however, a distinct chemical difference is found when the wood turpentine is treated by the sulphuric acid method. The following table shows the per cent rise in temperature compared to spirits of turpentine, of four samples tested by the author when subjected to this test as well as other results obtained on the same materials.

Specific Gravity.	Boiling Point.	Per Cent Rise with H_2SO_4 Compared to Turpentine.
Sample No. 1 — .862	159° C.	75.44
Sample No. 2 — .863	156° C.	74
Sample No. 3 — .863	158° C.	65.6
Sample No. 4 — .864	156° C.	97.6

1. Odor resembled pine needles.

2. Odor same as No. 1, but stronger.

3. Odor stronger than No. 2, with penetrating odor similar to formaldehyde and leaving a residual odor of cresote on evaporation.

4. Odor in bulk practically the same as spirits of turpentine, but that left after evaporation slightly stronger.

Of the above, these results show Nos. 1, 2, and 3 different to a considerable degree from turpentine. The action is a negative rather than a positive one, and because No. 4 gives nearly the same rise in temperature as does turpentine, it cannot be stated absolutely that it is nearly the same chemically, although such is very probably the case. The chemistry of the terpenes is not very well understood at present, and all the reactions that take place on the addition of concentrated sulphuric acid cannot be stated with certainty.

American turpentine consists largely of pinene ($C_{10}H_{16}$), which is converted into camphene ($C_{10}H_{16}$) by concentrated sulphuric acid, and this in turn is converted into polymeric modifications of the formulæ $C_{15}H_{24}$, and $C_{20}H_{32}$ (colophene). The reaction is undoubtedly much more complicated when this method is used than above stated, the large amount of sulphuric causing decomposition.

Dipentene, a constituent of Russian and Swedish turpentine, is produced by heating terpenes to a high temperature and is a product in the distillation of pine roots. It is formed in American turpentine by heating to 250° C.–270° C., as well as by the action of dilute sulphuric acid. Sylvertrene is also formed by the distillation of pine roots.

To return to wood turpentine, assuming that it differs in some respects from spirits of turpentine, the question arises of what this difference consists. It is obviously impossible for the commercial chemist to take up this subject in the laboratory and it must be left to the research laboratory to be discovered, while even here it may be impossible to determine until the chemistry of the terpenes is more thoroughly understood than at present. In the meantime conjectures as to the probable difference between these articles may be indulged in, and the author offers the following to explain the difference in composition between them: —

First, there is the possible presence of creosote,

ketones, acetone, etc., if the product is not carefully prepared, but these are not liable to occur in an article carefully manufactured, except in traces. The most acceptable explanation is that wood turpentine contains less pinene than spirits of turpentine, and a greater amount of terpenes of isomeric and polymeric composition. In support of this can be offered the formation, as given above, of dipentene by heating turpentine to 250° C. Now, of the four samples examined, No. 4 was produced at a low temperature by the latest machinery. Nos. 1, 2, and 3 were produced at a higher temperature, although how high the author is unable to say. Again, if the heat generated by the addition of concentrated sulphuric acid is caused by the transformation of pinene into polymeric modifications, it would follow that if this transformation had already taken place to some extent the heat developed on the addition of the acid would be decreased, which is found to be the case.

Parties manufacturing samples Nos. 1, 2, and 3 offer them for sale as a pure turpentine, differing only from American turpentine in odor, due to the process by which they are made. As regards sample No. 4 it would seem that with a little more care this product could be made identical with American turpentine, in which case parties manufacturing it have a perfect right to sell it as such.

As regards its use in adulterating turpentine, it

would seem that the probability of this is at present overestimated. The majority of these products could not be used with turpentine in sufficient quantities to pay without their presence being detected. If one can be produced pure enough to sell without question as American turpentine it should command the same price.

Benzole, Ninety per Cent. — Benzole is a by-product in the destructive distillation of coal. Ninety per cent benzole is so-called because 90 per cent is distilled before the temperature rises above 100° C. The average percentage of constituents of a good quality is about 70 per cent benzene, 24 per cent toluene, including a little xylene, and from 4 to 6 per cent of light hydrocarbons and carbon disulphide.

The compound benzene (C_6H_6), the lowest member of the benzene series of hydrocarbons, should not be confused with benzine derived from petroleum, from which it is entirely different. Treated with a cooled mixture of concentrated H_2SO_4 and HNO_3 at a temperature below 50° C., it is converted into nitro-benzene or oil of myrbane. On treatment with nascent hydrogen, generated by the action of HCl on iron filings, this is converted into aniline which enters largely into the manufacture of many artificial dyes.

Benzole is a clear, water-white liquid, flashing at ordinary temperature and having a peculiar characteristic odor. It is an excellent solvent for

many gums, oils, and waxes. It finds its chief use in the paint trade as a constituent of paint and varnish remover.

Benzine, 63°. (See Turpentine.)

APPENDIX

PIGMENTS RARELY ENCOUNTERED

Lithophone. — A combination of zinc sulphide (with small amounts of oxide) and sulphate of barium, made by adding solutions of $ZnSO_4$ and BaS, of such strength as to completely precipitate one another. The grade usually found on the market and considered standard contains about 65 per cent $BaSO_4$, the remainder being ZnS with small amounts of ZnO.

Lithophone is very white and has good body, but is not popular owing to the fact that it cannot be used in conjunction with lead in any form without the possible formation of the black PbS. As lead exists in some form or another in practically all varnishes, driers, and japans the use of lithophone is very limited. Its presence can always be detected (in the absence of ultramarine) by the evolution of H_2S gas on the addition of acid.

The determination of bases present as well as SO_3 may be made in the same manner as in the analysis of white paints. Determine sulphur by oxidizing with fuming nitric acid in a closed flask. Add some NaCl and HCl and evaporate the excess of nitric acid. Dilute, filter, heat, and precipitate with a hot solution of $BaCl_2$. After subtracting any sulphates previously obtained, calculate remainder

to ZnS, all remaining zinc being expressed as ZnO.

Paris Green [$3CuOAs_2O_3Cu(O_2H_3O_2)_2$]. — A combination of copper and arsenic having a very bright shade but deficient in body and tinting power. On this account, combined with the fact that it is extremely poisonous, its use is at present practically limited to that of a germicide. Its purity may be tested by NH_4OH, in which it is completely soluble to a blue solution.

Zinc Chromate ($ZnCrO_4$). — A very light yellow with a decided greenish cast. It has not the value of lead chromate and is more difficult and expensive to make. The solution must be neutral in reaction after precipitation, to make it complete. Its analysis may be made in the same manner as lead chromate.

Barium Carbonate ($BaCO_3$) is being used by at least one manufacturer in the production of paste and liquid paints. Its presence might be mistaken for whiting if the flame test were not applied on original sample, or it might be precipitated with H_2SO_4 and be mistaken for lead. Its occurrence in samples is so rare that most chemists may never encounter it. If sulphate of lead or calcium are present certain amounts of $BaCO_3$ will be precipitated as $BaSO_4$, and this will not carry through with calcium. In the samples encountered by the author it was used in conjunction with zinc oxide alone. The small amount of $BaSO_4$ left insoluble

was considered as precipitated by the sulphate in the zinc calculated to $BaCO_3$ and added to the remainder found.

To determine $BaCO_3$, precipitate with ammonia and ammonium carbonate, after all lead and third-group metals have been precipitated by NH_4OH and H_2S. Any calcium present will be precipitated in conjunction with it. Filter on Gooch crucible, dry, heat gently, adding small quantities of ammonium carbonate to convert any CaO formed to $CaCO_3$. Weigh combined carbonates, dissolve in HCl, filter out asbestos and precipitate barium with very dilute H_2SO_4 hot. Decant, boil with water to which a small quantity of HCl is added to dissolve any $CaSO_4$ precipitated, decant and repeat, finally washing $BaSO_4$ on filter with boiling water until free from acid. Dry, ignite, and weigh as $BaSO_4$ and calculate to $BaCO_3$, obtaining calcium as $CaCO_3$ by subtracting from total previously found.

TABLE I.

ATOMIC WEIGHTS

OF THE PRINCIPAL ELEMENTS.

Name	Symbol	Atomic Weight	Name	Symbol	Atomic Weight
Aluminium	Al	27.1	Lithium	Li	7.03
Antimony	Sb	120.2	Magnesium	Mg	24.36
Arsenic	As	75.0	Manganese	Mn	55.0
Barium	Ba	137.4	Mercury	Hg	200.0
Bismuth	Bi	208.5	Molybdenum	Mo	96.0
Boron	B	11.0	Nickel	Ni	58.7
Bromine	Br	79.96	Nitrogen	N	14.04
Cadmium	Cd	112.4	Oxygen	O	16.0
Calcium	Ca	40.1	Phosphorus	P	31.0
Carbon	C	12.0	Platinum	Pt	194.8
Chlorine	Cl	35.45	Potassium	K	39.15
Chromium	Cr	52.1	Silicon	Si	28.40
Cobalt	Co	59.0	Silver	Ag	108.0
Copper	Cu	63.6	Sodium	Na	23.05
Fluorine	F	19.0	Strontium	Sr	87.6
Gold	Au	197.2	Sulphur	S	32.06
Hydrogen	H	1.008	Tin	Sn	119.0
Iodine	I	127.0	Uranium	U	238.5
Iron	Fe	55.9	Zinc	Zn	65.4
Lead	Pb	206.9	Zirconium	Zr	90.6

TABLE II.

MOLECULAR WEIGHTS.

Calculated on basis of O = 16. H = 1.

NAME.	CHEMICAL FORMULA.	MOLECULAR WEIGHT.
Alum	$K_2Al_2(SO_4)_4 + 24H_2O$	948.74
Aluminium oxide	Al_2O_3	102.20
" hydroxide	$Al_2(OH)_6$	156.20
" sulphate	$Al_2(SO_4)_3$	342.38
Ammonium hydroxide	NH_4OH	35.04
" chloride	NH_4Cl	53.49
Barium oxide	BaO	153.40
" carbonate	$BaCO_3$	197.40
" chloride	$BaCl_2 + 2H_2O$	244.30
" hydroxide	$Ba(OH)_2$	171.40
" sulphate	$BaSO_4$	233.46
Calcium carbonate	$CaCO_3$	100.10
" oxide	CaO	56.10
" sulphate	$CaSO_4$	136.16
Bichromate of soda	$Na_2Cr_2O_7$	262.30
" " potash	$K_2Cr_2O_7$	294.50
Chromate of soda	Na_2CrO_4	162.20
" " potash	K_2CrO_4	194.40
Chromic oxide	Cr_2O_3	152.20
Ferric chloride	Fe_2Cl_6	324.50
" oxide	Fe_2O_3	159.80
" sulphate	$Fe_2(SO_4)_3$	399.98
Ferrous sulphate	$FeSO_4$	151.96
Lead carbonate	$PbCO_3$	266.90
" chloride	$PbCl_2$	277.80
" chromate	$PbCrO_4$	323.00
" hydroxide	$Pb(OH)_2$	240.90
White lead (basic carbonate)	$2PbCO_3Pb(OH)_2$	774.70
Lead oxide (litharge)	PbO	222.90
" oxide (red lead)	Pb_3O_4	684.70
" sulphate	$PbSO_4$	302.96
Magnesium carbonate	$MgCO_3$	84.36
" oxide	MgO	40.36
" pyrophosphate	$Mg_2P_2O_7$	222.72
Manganese dioxide	MnO_2	87.00
" pyrophosphate	$Mn_2P_2O_7$	284.00

TABLE II.—*Continued.*

NAME.	CHEMICAL FORMULA.	MOLECULAR WEIGHT.
Potassium chlorate	$KClO_3$	122.60
" cyanide	KCN	65.19
" hydroxide	KOH	56.15
" iodide	KI	166.15
" oxide	K_2O	94.30
" permanganate	$KMnO_4$	158.15
" platinic chloride	K_2PtCl_6	485.80
" sulphate	K_2SO_4	174.36
Silica	SiO_2	60.4
Sodium bicarbonate	$NaHCO_3$	84.05
" carbonate	Na_2CO_3	106.10
" chloride	NaCl	58.50
" hydroxide	NaOH	40.05
" oxide	Na_2O	62.10
" sulphate	Na_2SO_4	142.16
" thio-sulphate	$Na_2S_2O_3+5H_2O$	248.22
Zinc carbonate	$ZnCO_3$	125.40
" chloride	$ZnCl_2$	136.30
" oxide	ZnO	81.40
" sulphate	$ZnSO_4$	161.46
" sulphide	ZnS	97.46

ACIDS.

NAME.	CHEMICAL FORMULA.	MOLECULAR WEIGHT.
Acetic	$HC_2H_3O_2$	60.00
Carbonic (anhydride)	CO_2	44.00
Hydrochloric	HCl	36.45
Hydrobromic	HBr	80.96
Hydroiodic	HI	128.00
Hydrosulphuric	H_2S	34.06
Nitric	HNO_3	63.04
Oxalic	$H_2C_2O_4+2H_2O$	126.00
Sulphuric	H_2SO_4	98.06
" (anhydride)	SO_3	80.06
Sulphurous	H_2SO_3	82.06

TABLE III.

FACTORS.

One Per Cent of	Is Equivalent to	One Per Cent of	Is Equivalent to
Al_2O_3	1.5285 % $Al_2(OH)_6$	Cr_2O_3	1.3153 % CrO_3
Al_2O_3	3.3492 " $Al_2(SO_4)_3$	$PbCrO_4$ ..	.4060 " $Na_2Cr_2O_7$
Al_2O_3	9.2831 " Alum	$PbCrO_4$ ..	.4557 " $K_2Cr_2O_7$
$BaSO_4$ ...	.8922 " $BaCl_2$	Fe_2O_3	.7000 " Fe
$BaSO_4$ ...	.8455 " $BaCO_3$	Fe_2O_3	.9000 " FeO
$BaSO_4$ ...	.6618 " BaO	$PbSO_4$ ...	.6830 " Pb
$BaSO_4$ ...	.6089 " Na_2SO_4	$PbSO_4$ ...	.833 " Am. Ver.
$BaSO_4$ ...	1.2976 " $PbSO_4$	$PbSO_4$ ...	.8809 " $PbCO_3$
$BaSO_4$ ...	.5831 " $CaSO_4$	$PbSO_4$ ...	.8523 " White lead
$BaSO_4$ ...	.1373 " S	$PbSO_4$ ...	.7357 " PbO
$BaSO_4$ ...	.3430 " SO_3	$PbSO_4$ ...	1.0662 " $PbCrO_4$
$BaSO_4$ ...	.4201 " H_2SO_4	$PbSO_4$ ...	.753 " Pb_3O_4
$BaSO_4$ ...	.6916 " $ZnSO_4$	$PbSO_4$ ...	.4494 " $CaSO_4$
CaO	2.4271 " $CaSO_4$	$PbSO_4$ ...	.7705 " $BaSO_4$
CaO	1.7840 " $CaCO_3$	$PbSO_4$ ...	.5329 " $ZnSO_4$
$CaCO_3$...	1.3602 " $CaSO_4$	$Mg_2P_2O_7$.	.7575 " $MgCO_3$
$CaSO_4$ ...	.7351 " $CaCO_3$	$Mg_2P_2O_7$.	.6396 " P_2O_5
$CaSO_4$ ...	2.2250 " $PbSO_4$	Na_2O	1.7086 " Na_2CO_3
CO_2	2.2750 " $CaCO_3$	Na_2O	1.2898 " NaOH
CO_2	8.8034 " White lead	NaOH ...	1.4020 " KOH
Cr_2O_3....	4.2444 " $PbCrO_4$	ZnO	.8034 " Zn
Cr_2O_3....	8.0200 " Am. Ver.	$ZnSO_4$ ...	.5041 " ZnO
Cr_2O_3....	1.9349 " $K_2Cr_2O_7$	$ZnSO_4$ ...	1.8763 " $PbSO_4$
Cr_2O_3....	1.7234 " $Na_2Cr_2O_7$		

TABLE IV.

OIL CONSTANTS.

Name of Oil.	Specific gravity at 15.5° C.	Flashing Point. Open tester ° C.	Grams Iodine absorbed by 100 grams oil. Iodine number.	Mgms. KOH necessary to saponify 1 gram oil. Saponification number.
Castor	.963 – .968	——	83.6	178
Cottonseed....	.9225 – .9236	——	106.8 – 110.1	193
Corn.....	.9215 – .924	245 – 49	115	191
Linseed	.9312 – .9334	295	170 – 187	191
Linseed, boiled	.9336 – .936	275	167 – 170	190
Mineral	Variable	——	12.8 – 26.1	No action
Lard..	.917	——	76.2	195
Menhaden....	.929 – .932	252 (winter strained)	156 – 160	190
Olive	.9145 – .9168	——	78.9 – 86.4	194
Rosin	.986	Variable	67.9	——

TABLE V.

TABLE OF EQUIVALENTS.

Centigrade ..... = F. − 32 x $\frac{5}{9}$.
Centigram ..... = 0.1543 grain.
Centimeter ..... = 0.3937 inch.
Cubic foot of water..... = 62.4 pounds.
Cubic foot of water..... = 7.48 gallons.
Dram (Apoth. or Troy)... = 3.9 grams.
Fahrenheit ..... = $\frac{C. \times 9}{5} + 32$
Foot..... = 0.3048 meter or 30.48 centimeters.
Gallon (U.S.) ..... = 3.785 liters.
Gallon of water (U.S.) ... = $8\frac{1}{3}$ pounds.
Gallon of water (Imperial) = 10 pounds.
Grain (Troy)..... = 0.0648 gram.
Gram ..... = 15.432 grains.
Inch ..... = 2.54 centimeters.
Meter ..... = 39.3704 inches.
Ounce (Avoirdupois)..... = 28.35 grams.
Ounce (Troy or Apoth.)... = 31.104 grams.
Pound (Avoirdupois)..... = 453.603 grams.

TABLE VI.

PRINCIPAL BASIC AND ACID RADICALS FOUND IN PAINTS.

H_2O	Cr_2O_3	MgO	ZnO	CN
Al_2O_3	Fe_2O_3	MnO_2	SiO_2	CrO_3
BaO	PbO	HgO	SO_3	S
CaO	Pb_3O_4	Na_2O	CO_2	

TABLE VII.

Specific Gravity of Sulphuric Acid at 60° F. compared to Water at 60° F.

Standard of The Manufacturing Chemists' Association of the U. S.

Bé.°	Sp. Gr.	Per cent H_2SO_4	Bé.°	Sp. Gr.	Per cent H_2SO_4	Bé.°	Sp. Gr.	Per cent H_2SO_4
66.	1.8354	93.19	34.	1.3063	39.92	17.	1.1328	18.71
65.75	1.8297	91.80	33.	1.2946	38.58	16.	1.1240	17.53
65.5	1.8239	90.60	32.	1.2832	37.26	15.	1.1154	16.38
65.25	1.8182	89.55	31.	1.2719	35.93	14.	1.1069	15.25
65.	1.8125	88.65	30.	1.2609	34.63	13.	1.0985	14.13
64.75	1.8068	87.81	29.	1.2500	33.33	12.	1.0902	13.01
64.5	1.8012	87.04	28.	1.2393	32.05	11.	1.0821	11.89
64.25	1.7957	86.33	27.	1.2288	30.79	10.	1.0741	10.77
64.	1.7901	85.66	26.	1.2185	29.53	9.	1.0662	9.66
63.	1.7683	83.34	25.	1.2083	28.28	8.	1.0584	8.55
62.	1.7470	81.30	24.	1.1983	27.03	7.	1.0507	7.45
61.	1.7262	79.43	23.	1.1885	25.81	6.	1.0432	6.37
60.	1.7059	77.67	22.	1.1789	24.61	5.	1.0357	5.28
59.	1.6860	75.99	21.	1.1694	23.43	4.	1.0284	4.21
58.	1.6667	74.36	20.	1.1600	22.25	3.	1.0211	3.13
57.	1.6477	72.75	19.	1.1508	21.07	2.	1.0140	2.08
56.	1.6292	71.17	18.	1.1417	19.89	1.	1.0069	1.02
55.	1.6111	69.65						
54.	1.5934	68.13						
53.	1.5761	66.63						
52.	1.5591	65.13						
51.	1.5426	63.66						
50.	1.5263	62.18						
49.	1.5104	60.75						
48.	1.4948	59.32						
47.	1.4796	57.90						
46.	1.4646	56.48						
45.	1.4500	55.07						
44.	1.4356	53.66						
43.	1.4216	52.26						
42.	1.4079	50.87						
41.	1.3942	49.47						
40.	1.3810	48.10						
39.	1.3679	46.72						
38.	1.3551	45.35						
37.	1.3426	43.99						
36.	1.3303	42.63						
35.	1.3182	41.27						

ALLOWANCE FOR TEMPERATURE.

At 10° Bé. .029° Bé. or .00023 sp. gr. for 1° F.
At 20° " .036° " " .00034 " " 1° F.
At 30° " .035° " " .00039 " " 1° F.
At 40° " .031° " " .00041 " " 1° F.
At 50° " .028° " " .00045 " " 1° F.
At 60° " .026° " " .00053 " " 1° F.
At 63° " .026° " " .00057 " " 1° F.
At 66° " .0235° " " .00054 " " 1° F.

TABLE VIII.

Specific Gravity of Nitric Acid at 60° F. compared to Water at 60° F.

Standard of the Manufacturing Chemists' Association of the U. S.

Bé.°	Sp. Gr.	Per cent HNO_3	Bé.°	Sp. Gr.	Per cent HNO_3	Bé.°	Sp. Gr.	Per cent HNO_3
10.	1.0741	12.86	40.	1.3810	61.38	44.5	1.4428	75.40
11.	1.0821	14.13	40.5	1.3876	62.77	45.	1.4500	77.17
12.	1.0902	15.41	41.	1.3942	64.20	45.5	1.4573	79.03
13.	1.0985	16.72	41.5	1.4010	65.67	46.	1.4646	81.08
14.	1.1069	18.04	42.	1.4078	67.18	46.5	1.4721	83.33
15.	1.1154	19.36	42.5	1.4146	68.73	47.	1.4796	85.70
16.	1.1240	20.69	43.	1.4216	70.33	47.5	1.4872	88.32
17.	1.1328	22.04	43.5	1.4286	71.98	48.	1.4948	91.35
18.	1.1417	23.42	44.	1.4356	73.67	48.5	1.5026	95.11
19.	1.1508	24.82						
20.	1.1600	26.24						
21.	1.1694	27.67						
22.	1.1789	29.07						
23.	1.1885	30.49						
24.	1.1983	31.94						
25.	1.2083	33.42						
26.	1.2185	34.94						
27.	1.2288	36.48						
28.	1.2393	38.06						
29.	1.2500	39.66						
30.	1.2609	41.30						
31.	1.2719	43.00						
32.	1.2832	44.78						
33.	1.2946	46.58						
34.	1.3063	48.42						
35.	1.3182	50.32						
36.	1.3303	52.30						
37.	1.3426	54.36						
38.	1.3551	56.52						
39.	1.3679	58.82						
39.5	1.3744	60.06						

ALLOWANCE FOR TEMPERATURE.

At 10°–20° Bé., $\frac{1}{30}$° Bé. or .00029 sp. gr. for 1° F.

At 20°–30° Bé., $\frac{1}{23}$° Bé. or .00044 " " 1° F.

At 30°–40° Bé., $\frac{1}{20}$° Bé. or .0006 " " 1° F.

At 40°–48.5° Bé., $\frac{1}{17}$° Bé. or .00084 " " 1° F

TABLE IX.

Specific Gravity of Hydrochloric Acid Solutions at 60° F. compared to Water at 60° F.

Standard of the Manufacturing Chemists' Association of the U. S.

Bé.°	Sp. Gr.	Per cent HCl.
1.	1.0069	1.40
2.	1.0140	2.82
3.	1.0211	4.25
4.	1.0284	5.69
5.	1.0357	7.15
6.	1.0432	8.64
7.	1.0507	10.17
8.	1.0584	11.71
9.	1.0662	13.26
10.	1.0741	14.83
11.	1.0821	16.41
12.	1.0902	18.01
13.	1.0985	19.63
14.	1.1069	21.27
15.	1.1154	22.92
16.	1.1240	24.57
16.5	1.1283	25.39
17.	1.1328	26.22
17.5	1.1372	27.07
18.	1.1417	27.92
18.5	1.1462	28.78
19.	1.1508	29.65
19.5	1.1554	30.53
20.	1.1600	31.45
20.5	1.1647	32.38
21.	1.1694	33.31
21.5	1.1741	34.26
22.	1.1789	35.21
22.5	1.1836	36.16
23.	1.1885	37.14
23.5	1.1934	38.26
24.	1.1983	39.41
24.5	1.2033	40.55
25.	1.2083	41.72
25.5	1.2134	43.40

ALLOWANCE FOR TEMPERATURE.

10°–15° Bé., $\frac{1}{40}$° Bé. or .0002 sp. gr. for 1° F.

15°–22° Bé., $\frac{1}{30}$° Bé. or .0003 sp. gr. for 1° F.

22°–25° Bé., $\frac{1}{28}$° Bé. or .00035 sp. gr. for 1° F.

TABLE X.

Specific Gravity of Acetic Acid at 15° C. compared to Water at 4° C.

Specific Gravity at 15° C.	Per Cent $C_2H_4O_2$	Specific Gravity at 15° C.	Per Cent $C_2H_4O_2$	Specific Gravity at 15° C.	Per Cent $C_2H_4O_2$
1.0007	1	1.0470	35	1.0729	69
1.0022	2	1.0481	36	1.0733	70
1.0037	3	1.0492	37	1.0737	71
1.0052	4	1.0502	38	1.0740	72
1.0067	5	1.0513	39	1.0742	73
1.0083	6	1.0523	40	1.0744	74
1.0098	7	1.0533	41	1.0746	75
1.0113	8	1.0543	42	1.0747	76
1.0127	9	1.0552	43	1.0748	77
1.0142	10	1.0562	44	1.0748	78
1.0157	11	1.0571	45	1.0748	79
1.0171	12	1.0580	46	1.0748	80
1.0185	13	1.0589	47	1.0747	81
1.0200	14	1.0598	48	1.0746	82
1.0214	15	1.0607	49	1.0744	83
1.0228	16	1.0615	50	1.0742	84
1.0242	17	1.0623	51	1.0739	85
1.0256	18	1.0631	52	1.0736	86
1.0270	19	1.0638	53	1.0731	87
1.0284	20	1.0646	54	1.0726	88
1.0298	21	1.0653	55	1.0720	89
1.0311	22	1.0660	56	1.0713	90
1.0324	23	1.0666	57	1.0705	91
1.0337	24	1.0673	58	1.0696	92
1.0350	25	1.0679	59	1.0686	93
1.0363	26	1.0685	60	1.0674	94
1.0375	27	1.0691	61	1.0660	95
1.0388	28	1.0697	62	1.0644	96
1.0400	29	1.0702	63	1.0625	97
1.0412	30	1.0707	64	1.0604	98
1.0424	31	1.0712	65	1.0580	99
1.0436	32	1.0717	66	1.0553	100
1.0447	33	1.0721	67		
1.0459	34	1.0725	68		

TABLE XI.

Specific Gravity of Caustic Soda Solution at 15° C. compared to Water at 4° C.

(LUNGE)

SPECIFIC GRAVITY AT 15° C.	PER CENT NaOH.	SPECIFIC GRAVITY AT 15° C.	PER CENT NaOH.
1.007	.61	1.220	19.58
1.014	1.20	1.231	20.59
1.022	2.00	1.241	21.42
1.029	2.71	1.252	22.64
1.036	3.35	1.263	23.67
1.045	4.00	1.274	24.81
1.052	4.64	1.285	25.80
1.060	5.29	1.297	26.83
1.067	5.87	1.308	27.80
1.075	6.55	1.320	28.83
1.083	7.31	1.332	29.93
1.091	8.00	1.345	31.22
1.100	8.68	1.357	32.47
1.108	9.42	1.370	33.69
1.116	10.06	1.383	34.96
1.125	10.97	1.397	36.25
1.134	11.84	1.410	37.47
1.142	12.64	1.424	38.80
1.152	13.55	1.438	39.99
1.162	14.37	1.453	41.41
1.171	15.13	1.468	42.83
1.180	15.91	1.483	44.38
1.190	16.77	1.498	46.15
1.200	17.67	1.514	47.60
1.210	18.58	1.530	49.02

TABLE XII.

Specific Gravity of Ammonia Solutions at 60° F. compared to Water at 60° F.

Standard of the Manufacturing Chemists' Association of the U. S.

Bé.°	Sp. Gr.	Per cent NH_3
10.	1.0000	.00
11.	.9929	1.62
12.	.9859	3.30
13.	.9790	5.02
14.	.9722	6.74
15.	.9655	8.49
16.	.9589	10.28
17.	.9524	12.10
18.	.9459	13.96
19.	.9396	15.84
20.	.9333	17.76
21.	.9272	19.68
22.	.9211	21.60
23.	.9150	23.52
24.	.9091	25.48
25.	.9032	27.44
26.	.8974	29.40
27.	.8917	31.36
28.	.8861	33.32
29.	.8805	35.28

ALLOWANCE FOR TEMPERATURE.

Correction to be subtracted from each degree above 60° F.

Degrees Baumé	70° F.	80° F.	90° F.	100° F.
14°	.020° Bé.	.022° Bé.	.024° Bé.	.026° Bé.
16°	.026° "	.028° "	.030° "	.032° "
18°	.031° "	.033° "	.035° "	.037° "
20°	.037° "	.038° "	.040° "	.042° "
22°	.043° "	.045° "	.047° "	
26°	.057° "	.059° "		

TABLE XIII.

Specific Gravity of Ethyl Alcohol and Percentage by Weight at 15° C.

(FOWNES)

SPECIFIC GRAVITY AT 15° C.	PER CENT C_2H_6O BY WEIGHT	SPECIFIC GRAVITY AT 15° C.	PER CENT C_2H_6O BY WEIGHT	SPECIFIC GRAVITY AT 15° C.	PER CENT C_2H_6O BY WEIGHT
.9981	1	.9490	35	.8745	69
.9965	2	.9470	36	.8721	70
.9947	3	.9452	37	.8696	71
.9930	4	.9434	38	.8672	72
.9914	5	.9416	39	.8649	73
.9898	6	.9396	40	.8625	74
.9884	7	.9376	41	.8603	75
.9869	8	.9356	42	.8581	76
.9855	9	.9335	43	.8557	77
.9841	10	.9314	44	.8535	78
.9828	11	.9292	45	.8508	79
.9815	12	.9270	46	.8483	80
.9802	13	.9249	47	.8459	81
.9789	14	.9228	48	.8434	82
.9778	15	.9206	49	.8408	83
.9766	16	.9184	50	.8382	84
.9753	17	.9160	51	.8357	85
.9741	18	.9135	52	.8331	86
.9728	19	.9113	53	.8305	87
.9716	20	.9090	54	.8279	88
.9704	21	.9069	55	.8254	89
.9691	22	.9047	56	.8228	90
.9678	23	.9025	57	.8199	91
.9665	24	.9001	58	.8172	92
.9652	25	.8979	59	.8145	93
.9638	26	.8956	60	.8118	94
.9623	27	.8932	61	.8089	95
.9609	28	.8908	62	.8061	96
.9593	29	.8886	63	.8031	97
.9578	30	.8863	64	.8001	98
.9560	31	.8840	65	.7969	99
.9544	32	.8816	66	.7938	100
.9528	33	.8793	67		
.9511	34	.8769	68		

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